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The moisture gradient and its effect in the drying of clayware

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NOTE TO USERS

THE MOISTURE GRADIENT AND ITS EFFECT IN THE DRYING OF CLAYWARE

by

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Nomenclature

a = Thermal coefficient of expansion.

b = The ordinate intercept for a straight line.

$\mathfrak{C}$ = Subscript referring to centerline conditions.

E = Modulus of elasticity in psi.

f = Subscript referring to final conditions.

$f(r)$ = Some function of the radius of a drying sphere for expressing modulus of elasticity.

I = Moment of inertia for flexural tests in $(\text{inches})^4$.

L = Length of bar in flexural tests in inches.

m = Slope of any straight line plot.

M = Moisture content in % H_2O (Dry Basis).

$M_{\mathfrak{C}}$ = Moisture content in % H_2O (Dry Basis) at the center line of the drying body.

M_s = Moisture content in % H_2O (Dry Basis) at the surface of the drying body.

o = Subscript referring to original conditions.

P = Load in flexural tests in pounds.

r = Radius of a sphere in inches.

S_r = Radial stress in psi.

S_t', S_t = Tangential stresses in psi.

t = Time of drying.

T = Temperature.

u = Radial displacement of a point due to stress and shrinkage.

x = Distance from drying surface toward the center of the drying body.

1 = Subscript referring to a particular value of the variable with which it is used.

Δ = Deflection of the cylindrical bar in flexural tests in inches.

ϵ_r = Unit displacement of a point in drying ware in the radial direction.

ϵ_s = Unit displacement of a point in drying ware due to shrinkage with respect to the center of the ware.

ϵ_t = Unit displacement of a point in drying ware in the tangential direction.

μ = Poisson's ratio

π = A constant = 3.1416

I. INTRODUCTION

start

At least some of the problems encountered in the drying of ceramic ware are as old as the ceramic art itself, and that age can be counted off in terms of centuries. In the past fifty years a great deal of progress has been made toward finding the explanations for the behavior of clays during the various processes through which they must pass in order to emerge as dinnerware, vases, structural clay products and many other useful articles.

The drying process has been studied from many viewpoints, and in the course of those studies much has been learned about the inner mechanisms involved, and many new methods of drying as well as improvements on old methods have been developed.

There are, however, many conflicting opinions to be found at present concerning the probable behavior of the clay-water system during the drying operation. One phenomenon which occurs entirely too often is that of cracking of the ware due to improper drying conditions.

stop

It was the purpose of this work to study the drying conditions for clayware with the aim of finding a method for predicting the maximum safe moisture gradient that the clay can withstand by correlation of moisture content with the stress-strain properties of the wet body. The term maximum safe moisture gradient as used above would lead ultimately to a

prediction of the maximum safe rate of drying (i.e. the highest rate of water removal that can be accomplished without cracking the ware.) The following sections will outline how this was to be done.

An initial decision was made to confine this study to the behavior of a commercially prepared clay body[1] in the belief that by so doing, the conditions would more closely compare with those found in industry, and the results and conclusions would be directly applicable to the problems arising daily in industrial manufacture of ceramic ware.

The other alternative would have been to make the observations on a pure clay mineral such as kaolinite. This would have the advantage of elimination of any variables introduced by the usual addition of flint and feldspar as inert materials. The results might have been easier to correlate due to the reduction in the number of variables, but since pure kaolinite is not used alone commercially, the same results would not necessarily be obtained with the clay body preparations.

An attempt was made to compensate for the possible disadvantages of the chosen body by ordering a large enough quantity of the mixture to be able to use the same composition for all tests. In addition, the same batch of clay was

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[1]The clay used was a typical hotel china body supplied by Buffalo Pottery, Inc. of Buffalo, New York.

re-used for different tests in order to further eliminate possible change in variables such as body analysis, particle size and amount and kind of electrolyte present.

II. THEORY

A great deal has been written about the physical mechanism involved in the drying of various bodies. It is not the intention here to give a complete review of the subject but rather to limit the discussion to those factors generally believed to influence the behavior of fine grained substances such as the commercially prepared clay body studied here.

As mentioned previously there is a difference of opinion by different authorities on the exact mechanism by which water moves from the interior of a body to its surface during the drying operation. Sherwood and Comings[1] believe that there are three distinct stages in the drying of clays: (1) a constant rate period in which the drying surface is completely wet and the amount of water removed per unit of time and per unit of drying area is a constant, (2) a falling rate period in which surface evaporation controls (the so-called "zone of vaporization" remains at the drying surface though the "wet" surface continually diminishes in area) and (3) a falling rate period in which internal liquid diffusion controls.[2]

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[1] Sherwood, T. K. and Comings, E. W., "The Drying of Solids", Ind. Eng. Chem., 25, 311-5 (1933).

[2] In this period the "zone of vaporization" recedes into the drying body for porous or granular materials but is thought to remain at the drying surface for most clays due to the fine particle size of the clay and the resistance to moisture flow thus caused.

Morgan and Hursh[1] disagree with the concept of three distinct stages in drying as offered by Sherwood. They state that the drying takes place in two essential stages with the division point occurring at the point defined as the surface shrinkage limit. This point represents the condition of the clay when the surface has shrunk to approximately its final dimensions. If there is a finite moisture gradient, as there almost always is in drying, the center of the piece may still be undergoing shrinkage when the surface shrinkage limit has been reached. The first stage of drying is said to be controlled by the rate of evaporation from the surface which in turn is controlled by the difference between the vapor pressure of the liquid in the clay and the vapor pressure in the surrounding air stream.

In the stage of drying occurring after the surface shrinkage limit is passed, the controlling factors are said to be a combination of liquid and vapor diffusion to the surface.

On the other hand, Ceaglske and Hougen[2] state that the driving force causing water to flow to the surface, there to be evaporated in the drying operation, is a force of capillarity for granular solids. This they maintain is a much

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[1]Morgan, W. R. and Hursh, R. K., "Conditions Governing Diffusion of Water in Clays", Jour. Amer. Ceram. Soc., 22, 271-8 (1939).

[2]Ceaglske, N. H. and Hougen, O. A., "Drying of Granular Solids", Ind. Eng. Chem., 29, 805-13 (1937).

sounder basis for the calculation of moisture distribution and drying rates than the method based on diffusion. They state that water will flow to regions of highest capillarity, regardless of concentration, and experimental data are cited to back up this statement. The following is quoted, however, from the same article by Ceaglske and Hougen[1].

> The diffusion equations apply only if the capillary tension producing flow varies directly with the unsaturation of the solid, where the body is uniform in composition and where the gravitational effect is negligible. Possibly such a situation is approximated in fine fibrous structures or even in fine clays.

This statement admits that diffusional relations may satisfactorily express the behavior of the clay-water system but implies that an approach to the problem based on capillarity is more universally applicable to drying problems including the drying of clays.

Sherwood[2], in a later article, makes the statement that the frequent agreement of drying data with the integrated diffusion equations may be largely fortuitous.

To use the capillarity calculations for the determination of moisture distribution it is first necessary to know the magnitude of the suction produced in the solid by

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[1] Ibid, p. 806.

[2] Sherwood, T. K., "The Air Drying of Solids", Trans. Amer. Inst. Chem. Engrs., 32, 156 (1936).

interfacial tension. To do this Ceaglske and Hougen used a method developed by Haines[1] in which a thin layer of a granular solid was placed on a sealed filter paper in a Buchner funnel 9 cm. in diameter and connected with a burette manometer. The apparatus was filled with water, and by adjusting the height of the burette in small steps, a given series of suction values was obtained. However, according to Haines, this method works satisfactorily for clay only in the range corresponding to the early stages of drying. After this the suction values are too high for satisfactory measurement in this manner due largely to the very fine particle size of the clay. Hence, this particular method is not applicable to the present work.

A method has been developed by Macey[2] in which pressure versus equilibrium moisture content can be determined. The method employs a porous piston to which a given pressure is applied and maintained till equilibrium is reached. The clay is then removed from beneath the piston and its moisture content determined. The pressure and moisture content were found to be related by the expression $P = ae^{-\beta M}$ in which P is the pressure exerted by the piston, M is the moisture

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[1]Haines, W. B., "A Further Contribution to the Theory of Capillary Phenomena in Soil", Jour. Agr. Sci., 17, 264-90 (1927).

[2]Macey, H. H., "VI Clay-Water Relationships and the Internal Mechanism of Drying", Trans. Brit. Ceram. Soc., 41, 73-121 (1942).

content of the clay at equilibrium and α and β are constants depending upon the clay used. It was considered by Macey[1] that this pressure P was a measure of the force of repulsion between the surfaces of the clay particles at the moisture content M and constituted the driving force which caused water to flow to the surface during drying.

In the work of Macey just cited, use was made of the expression relating P and M and a similar one relating aqueous conductivity C and moisture content M ($C = \theta e^{\phi M}$ in which θ and ϕ are constants) in predicting moisture content distribution for drying from one face only. Good agreement was reported between calculated and experimental values.

Theoretical equations have also been given by Sherwood[2] for moisture distribution during the drying of infinite clay slabs with drying from one direction presumably. Two sets of equations are given: (1) moisture gradients during the constant rate period of drying in which it was found that the gradients tended to be parabolic in form no matter what the initial gradient may have been if the constant rate period was long enough and (2) moisture gradients assuming that a constant rate drying period was followed by a period in which internal diffusion was controlling. The latter case assumes

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[1]Ibid, p. 73.

[2]Sherwood, T. K., "The Drying of Solids - IV Application of Diffusion Equations", Ind. Eng. Chem., 24, 307-310 (1932).

that the gradient was parabolic in form at the critical moisture content when the internal diffusion became the controlling factor.

Since these equations are for application to infinite slabs they cannot be applied directly to the present work which involved the drying from all sides of two-inch cubes. In addition, no mention was made in the derivation of the equation for case (2) of the effect on moisture gradient of the first falling rate period in which surface evaporation controls.

For these reasons it was decided to make actual measurements of the moisture gradient existing in the clay cubes at the time surface cracks appeared and to use the experimental gradients in approximation of the drying stresses. This subject is taken up more fully under Results and Discussion.

Regardless of which mechanism, diffusion or capillarity, is the one governing movement of water to the surface in drying, one fact is clear. As the water content of the plastic clay mass is decreased, the clay shrinks from its original dimensions, and it is the amount of shrinkage and the manner in which this shrinkage occurs that is responsible for the formation of cracks during the drying operation.

As the drying operation proceeds, the outer surface becomes much drier than the plane just behind it and so on

toward the center of the ware so that a moisture gradient is set up between the drying surface and the interior. As the operation continues, the regions of lower moisture content have shrunk more than those of higher moisture content, and there is, in effect, an attempt to compress the wetter interior of the piece by the more rapidly shrinking outer shell. Since there is a definite limit which this compression cannot safely exceed, stresses are set up in the piece which will cause cracks to develop if water is not removed fast enough from the interior of the ware to allow it to shrink also.

Macey[1] has made the following statement:

> Cracking of clay articles during drying is ultimately due to moisture content gradients between their surface and interior. It has been shown how and why these gradients have been set up and how they may be calculated in the case of linear flow.
>
> It remains if possible to extend the calculations into two or three dimensions and to discover what are the maximum gradients a clay can withstand without cracking, and why, and how these gradients may be reduced and the drying strains alleviated, so that losses from this source may be diminished or rates of drying increased.

The particular type and percentage of clay mineral used in the body composition has much to do with the success or failure of the drying operation as far as cracking is concerned. The type and amount of electrolyte present is also important.

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[1]Macey, H. H., op. cit., 41, p. 120.

In general, the more plastic clays have the greater drying shrinkage[1]. Likewise, the body compositions with higher percentages of clay minerals generally have a greater shrinkage than those with low percentages of clay. Thus, because of higher shrinkage, use of either a more plastic clay or higher percentages of clay makes a body more susceptible to cracking in drying due to the tendency to cause greater strain between the surface and interior of the piece.

The more plastic clays usually have smaller sized particles than those which are less plastic. Likewise, an increase in the percentage of clay mineral used in the body has the effect of decreasing the average particle size for the material, because the clay particles tend to fill the voids between the larger particles of flint and feldspar used in most bodies. Thus, if the average particle size of the material is decreased by either method just discussed, those particles tend to form a more closely packed unit, and the water from the interior of the piece meets more resistance on its path to the surface in the drying operation. The result is a higher moisture gradient for given drying conditions and, therefore, greater susceptibility to cracking.

These variables were limited in the present work by use of only one batch of clay of a fixed body composition.

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[1]Norton, F. H., "Refractories", p. 143, 2d ed., New York, McGraw-Hill Book Company, Inc., 1942.

One variable was introduced, however, by the addition of 0.2% sodium silicate as described in the Apparatus and Procedure section. The clay as received was assumed to have calcium ions as the exchangeable ion in the structure, and this material is hereafter referred to as calcium clay. The addition of sodium silicate presumably causes the exchange of sodium ions for the calcium ions, and this material is therefore referred to as sodium clay.

The detailed theory of this exchange is long and complicated. Briefly, it involves the counterbalancing of the small negative electrical charges on the clay particles by preferential adsorption of the positively charged calcium or sodium ions. The extent to which this electrical counterbalancing is effective is dependent upon the charge, hydrated size and the number of so-called counter ions which are close enough to influence the particle. It is also necessary to consider the dielectric constant of the medium, which in this work was water.

The type of counter ions surrounding the clay particles has a direct effect on the force of attraction or repulsion between the particles, and thus directly affects the nature of the entire clay mass.

Clay particles with calcium as the counter ion tend to be attracted to each other and thus form aggregates composed

of a number of smaller units of the clay mineral. The result is that the calcium clay has a larger effective particle size, larger pore sizes between particles and will hold a greater amount of water while still remaining rigid.

Sodium clay particles, on the other hand, tend to repel each other more strongly and thus remain deflocculated as long as the over-all water content is high enough to permit that condition. The sodium clay particles are very small leaving small pore spaces and, consequently, a higher resistance to the flow of moisture to the surface in drying.

With these factors in mind, it is not unreasonable to expect that more difficulty should be encountered in the drying of sodium clays than in the drying of calcium clays, because the increased resistance to the flow of moisture to the surface causes a higher moisture gradient, higher unit strain and therefore higher stresses. This was borne out by experiment as is explained later.

The physical characteristics of the material used in this investigation have been discussed from the standpoint of their effect on the drying stresses.

The quotation from Macey on page 10 gives the primary reasons for the undertaking of the present work which is an attempt to evaluate more fully the factors setting up the

stresses during drying and to show how these factors are interrelated and how they may be determined.

III. APPARATUS AND PROCEDURE

A. Drying tests.

1. General.

A commercial hotel china body[1] as mentioned previously was used in this work. Tests were made in two series: (1) the body was used as supplied with only the addition of water to aid in forming the test specimens and (2) sodium silicate was added to the original clay mix in the amount of 0.2% on the basis of the dry weight of clay.

Since the object of this work was to evaluate the factors causing cracking, the drying conditions were deliberately made quite severe in order to cause the specimens to crack. With this in mind, considerable experimentation was necessary in order to find conditions suitable for the type of specimen used. All of the final tests to which consideration is given in this thesis were made on two-inch clay cubes. Some of these were dried from one face only, but most of them were dried from the five exposed faces when the specimen was placed on the balance pan in the drier. Drying conditions for almost all runs were maintained at 80°-85°C and approximately 7% relative humidity. Air velocity was approximately 20 feet per second. The air was recirculated by means of a

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[1] A typical commercial hotel china mix was supplied for this work by Buffalo Pottery, Inc. of Buffalo, New York.

motor-driven fan and external ducts. The primary purpose of the recirculation was to speed up the rate of drying by increasing the airflow over the specimen and to do so without loss of all the sensible heat in the airstream. It was thought desirable to have the equipment set up in such a manner that it would be possible to bleed out some of the hot air and let in some cold, less-humid air from the outside if the air humidity increased too much during the drying operation. It was later found that this feature was unnecessary due, probably, to the large volume of air handled in comparison with the size of the specimen and the amount of water to be removed from it.

The drier used in this work was an insulated rectangular box of 23 inches x 11 inches x 10 inches inside dimensions. The first drying tests were made using a small fan inside the box for air circulation so that the entire apparatus was a self-contained unit. The air velocity obtained in this manner proved to be inadequate to cause cracking, and the larger external fan was then installed. The air velocity was measured approximately with an anemometer type instrument placed at the position which the drying cube occupied in the actual tests.

The rate of heat loss from the fan and external piping was appreciable, but this work was carried on with the

only readily available equipment. Radiation losses from the ductwork were reduced greatly by wrapping thin aluminum foil around the piping.

The heating units in the drier itself included one 500 watt and two 300 watt elements. Two of these units were wired into the circuit directly, and the third was wired through a Cenco-De Khotinsky thermo-regulator in order to provide the necessary temperature control.

A small opening was made in the top of the drier to allow a wire to pass through on which was suspended a sheet metal pan holding the drying specimen. The wire was in turn fastened to one arm of a balance so that the progress of the water removal could be measured and the rate of drying computed.

One end of the drier was fitted with a double window so that the specimen could be observed visually during the test. This was a necessary condition, because it was desired to interrupt each drying run at the precise moment that a surface crack appeared on the specimen. To aid in the detection of the cracks during drying, a telescope was used to observe the drying surface.

The weight of the specimen was recorded at frequent intervals during the run. Graphs were plotted of weight against time, and drying rates in terms of grams of water

removed per unit area of drying surface per unit time were plotted against free moisture content. In almost all runs a short constant-rate period of drying was evident, but the cracks occurred during the falling-rate portion of the run.

A sample drying-rate curve is shown in the Appendix in Figure 15.

For each test, the initial moisture content of the specimen at the time it was placed in the drier was determined by weighing the cube before the drying run and after complete drying. This was accomplished by adding the dry weight of the moisture gradient samples (discussed below) to the dry weight of the remainder of the cube.

The moisture gradient existing in the clay piece during drying was considered to be of prime importance in causing the cracks developed in drying. For this reason, it was necessary to determine the gradient existing in the specimen at the time the first crack appeared. As soon as a small surface crack became visible the drying run was interrupted, and the specimen was removed from the drier. In most cases the cracks occurred near the center of one of the faces of the cube. Wet clay samples were desired which would most nearly represent the moisture gradient in a direction perpendicular to the surface on which the crack occurred.

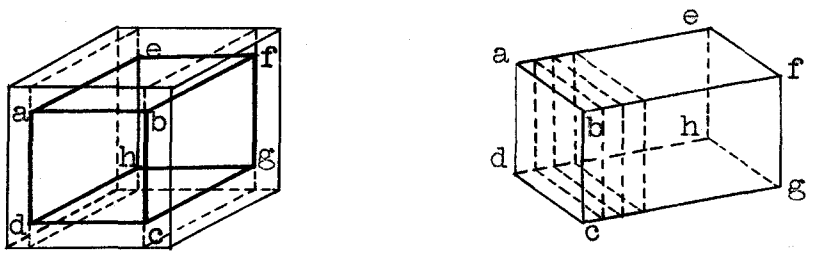

Figure 1. Method of obtaining moisture gradient samples.

Slices were cut from all four sides as indicated by the dotted lines in Figure 1-a and set aside in order to eliminate error from the fact that the drying tends to be faster on the corners due to evaporation from three surfaces compared with one surface at the center of the face of the cube. The remaining rectangular solid shown at the right in Figure 1-b was then cut into thin slices[1], the small samples weighed as quickly as possible and placed in an oven at 105°C for 24 hours or until dried to a constant weight. The per cent moisture was calculated on a dry basis for all tests in this work. Plots were made of per cent moisture as a function of distance

[1]These slices were made using a specially designed cutter which could be adjusted for a definite thickness of slice. Most of the samples were taken at 0.1 cm. intervals although Runs 38, 39 and 40 were taken at 1/16 inch intervals.

from the drying surface. An example of this is shown in the Appendix, and the effect of the moisture gradient is taken up more fully under Results and Discussion.

In the earlier runs, the wet clay samples used for moisture gradient determination were placed in crucibles for the weighing, drying and reweighing. In the later runs, these operations were carried out using covered weighing bottles to prevent loss of weight in the interval before the first weighing was made. It was felt that the latter tests were more accurate for this reason. Even though an error may have been introduced in measuring absolute moisture content using the crucibles, the over-all difference in water content from the surface to the center of the cube should be affected very little by the small loss of weight encountered before the weighing of the crucibles could be completed.

In most cases the cracks occurred near the center of one of the faces of the cube as previously mentioned, but in some cases they occurred at the corners of the cube and seemed to enter the cube at approximately a 45° angle. In these cases, further examination showed that all the corners tended to crack with the result that the remainder of the specimen took on a spherical shape. This observation has been noted by Norton[1] in the case of spalling and has been

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[1]Norton, F. H., "Refractories", 2d ed., Chap. XIV, New York, McGraw-Hill Book Company, Inc., 1942.

attributed to a shear failure of the material. The present case should be analogous with regard to type of failure. The number of failures that occurred in this manner in the present project was rather small.

2. Preparation of specimens for drying.

a. Calcium clay[1].

The calcium clay specimens were relatively easy to prepare. The body was used just as supplied with the exception that distilled water was added in order to obtain a mass of the right consistency for plastic molding. A plaster mold was prepared with a cubical cavity 2 inches on a side. The plastic clay was carefully worked into the mold to prevent any air bubbles from remaining in the specimen. When the mold was completely filled, it was turned over to remove the specimen which was then placed in a desiccator in which an atmosphere nearly saturated with water vapor was maintained. The specimen was allowed to remain under these conditions at least several hours or overnight in order to alleviate any stresses set up in the forming operation and to allow the moisture content to come to an equilibrium value throughout. The cube was then considered ready to be placed in the drier and tested as described.

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[1]See p. 12 for definition.

b. Sodium clay[1].

It was noted in the early tests on the calcium clay that the drying conditions being used rarely if ever caused cracking. It was finally decided, at the suggestion of Dr. A. L. Johnson[2], that the same conditions be employed in drying clay samples to which had been added a small amount of sodium silicate. A test run was made using the same clay as before to which had been added 0.2% sodium silicate. Under identical drying conditions cracks were developed in this sample. Accordingly, a larger batch of clay was mixed and 0.2% sodium silicate by weight was added to the plastic mass. As expected, the clay became deflocculated and appeared fluid[3]. In order to obtain a cubical sample for drying it was necessary to make a casting in a plaster mold. This was done according to standard casting procedure except that the mold had to remain unopened for a longer period of time than normal in order to allow the slip to set sufficiently. The reason was that the two-inch thickness was greater than is encountered in normal casting procedure. It was found that a two-hour period was sufficient time to allow the specimen

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[1]Ibid.

[2]Dr. A. L. Johnson was formerly Professor of Ceramic Engineering at Iowa State College and was the faculty adviser for this project.

[3]See p. 12-3 for a discussion of the theory for this reaction.

to become rigid enough to support its own weight when removed from the mold. A greater time might have been advisable if the specimen were to be used for other purposes, but in this procedure it was desired to start the drying run at as high an initial moisture content as possible.

The specimens, on removal from the molds, were placed in the desiccator just as the calcium clay specimens were. This step was necessary in the case of the sodium clay because of the moisture gradient present in the specimen as a result of the casting process, and the necessity for allowing the gradient to be at least partially dissipated before the start of the drying run. On removal from the molds the clay cubes were quite soft and wet in the center and much less wet on the outer surfaces due to water removal by the plaster. This gradient was in the same direction as the one caused in drying. If the gradient was not large when the drying run was started, its effect was considered to be negligible in comparison with that caused by water removal in the drier.

Procedure from this step on was the same for the sodium and the calcium clay.

3. Unidirectional drying.

a. Use of specimens coated with Tygon paint.

At the beginning of the project, it was felt

that data on moisture gradients in particular would be more precise if the drying were carried out under controlled conditions with the specimens being dried from one face only. This hypothesis proved to be correct and would have been quite useful except for one flaw. The cylindrical bars first tested and later the cubes dried from one face only failed to crack. The gradients were of the same order of magnitude, and shrinkage took place first at the surface just as in the tests in which the pieces were dried from all sides, but the stresses of sufficient magnitude to cause cracking were absent due to the uniaxial strain conditions as compared with triaxial strain to which the cubes were subjected in drying from all sides.

However, this series of runs was interesting for another reason. It was found that the clay pieces could be coated with a clear Tygon[1] paint (TP-217) and dried from one surface quite successfully. Little moisture was lost through the Tygon coating, and the moisture gradients obtained from the clay specimens were believed to be quite accurate and uniform. In this work wet clay bars 7/8 inch in diameter and approximately 8 inches long were dipped into the paint and then suspended in air to dry. The surface of the paint was dry to the touch after five to ten minutes at atmospheric

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[1]Tygon paint was supplied by U. S. Stoneware Co., Akron, Ohio.

conditions, and the bars were dry enough to handle at the end of an hour. The bars were completely coated in the dipping process by dipping one end and waiting ten to fifteen minutes for it to dry enough so that the other end could be dipped.

After a 48-hour period to allow the moisture to come to equilibrium throughout the specimen, a thin slice was removed from one end of the cylinder, and the specimen was then placed in the drier under approximately the same conditions described previously. It was found that the cylindrical bars and also the two-inch cubes when dried from one face only could be dried completely without cracking using the same conditions which habitually cracked the specimens dried from all sides. The total drying time required was greater for unidirectional drying, thus placing an economic limitation on this method if used commercially.

The Tygon coating was easily stripped from the specimens when they were removed from the drier for moisture gradient determination.

A Tygon top coating (TP-11, gray) was also tried but was not as satisfactory for this work as the clear coating because of a lesser resistance to high temperatures.

One Tygon coated cylinder inadvertently left in a drawer for a period of nine months was found to be still

soft and plastic indicating little if any water loss in that period.

The Tygon paint did tend to become slightly sticky when heated in the drier to 90°C or above.

B. Tensile tests.

Although ceramic articles are normally not used in situations which place them under tension, it was necessary in the present work to know the ultimate tensile strength of the clay body used. This was essential because cracking failures are normally failures in tension as pointed out in the Thermal Stress Analogy section of Results and Discussion.

In fact, it was necessary to know the ultimate tensile strength of the clay over quite a range of moisture content. No standard test procedure was known for this material and this set of conditions. Therefore, it was decided to adapt the A.S.T.M. standard tensile test for hydraulic-cement mortars (A.S.T.M. designation: C 190-44) to meet the requirements. This was accomplished with minor modifications in the preparation of the test samples.

The briquet gang mold recommended for preparation of the mortar specimens was used here. The clay was mixed with water until a plastic mass was achieved. This was tamped

into the mold in much the same manner as recommended for the mortar, using the thumbs to work the clay into the corners and to eliminate any entrapped air. Finally, the top surface of the specimen was smoothed off with a spatula which had been moistened with water to prevent it from sticking to the clay. The specimens were then partially air-dried in a moist atmosphere in order to get a slow rate of drying and leave the entire specimen at nearly the same moisture content. This procedure was necessary because the specimens were to be tested at varying moisture contents, and the best way to obtain them was to interrupt the drying operation on different groups of samples at different times. When the specimens were removed from the molds, they were placed in a moist atmosphere for a short period of time in order to allow the moisture content to equalize throughout the specimen cross-section. The specimens were then tested in a standard testing machine in which the loading was accomplished by adding shot to a tared bucket. The load at the time the test specimens ruptured was recorded, and a sample of clay was taken at the fracture for a moisture determination. The moisture content was obtained by drying the sample in an oven at 105°-110°C until a constant weight was recorded.

Since the clay shrinks on drying it was necessary to make actual measurements with a micrometer caliper of the cross-section at the fracture to use in determination of the

ultimate tensile strength.

A plot was made of ultimate or breaking tensile strength against moisture content as shown in Figure 2 for the sodium clay and for the calcium clay.

In making the calculations for ultimate tensile strength a correction factor was applied in order to compensate for the stress concentration[1] caused by the shape of the briquet. Extremely low values of ultimate strength were discarded either because of air-holes or faults in the specimen or because of an assumed eccentricity of loading in the testing machine. Ample proof of inaccuracy of the lower values in similar testing of cement mortars due to eccentricity of loading is offered by Evans[2]. He showed that the strain caused by the loading was often appreciably different on opposite sides of the briquet. This caused the specimen to be under a much greater stress on one side than on the other with the result that the specimen failed sooner than expected.

C. Modulus of elasticity tests.

The plot of modulus of elasticity (E) as a function of per cent water shown in Figure 5 was obtained from a series

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[1]See Tensile Tests under Results and Discussion.

[2]Evans, R. H., "Extensibility and Modulus of Rupture of Concrete", The Structural Engineer, 24, 636-59 (1946).

of flexure tests on cylindrical specimens 7/8 inch in diameter. Most of the specimens were ten inches in length, but several of those used in earlier runs were about eight inches long. It was felt that the longer specimens would give a more positive beam action, particularly for those runs at a low moisture content.

The solid cylindrical bars were extruded from a small hand auger at about 20 - 25% H_2O. These bars were immediately placed in the drying cabinet (described under Drying Tests), which was at this time being operated as a desiccator for storing and aging of the clay samples. The temperature was maintained constant at about 25°C, and the humidity was held constant by blowing air across a pan of water placed in the cabinet. Under these conditions the bars seemed to dry very slowly. The samples removed first were those at high moisture content. For the runs at lower water content a preliminary drying operation was carried out after which the bars were left at the conditions described above in order to bring the entire cross-section of the bar to constant equilibrium moisture conditions before the flexure test was conducted.

The bars were suspended between two rounded bearing blocks set exactly ten inches apart.[1] The loading was

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[1]The distance between the beam supports in the earlier runs was 8.4 inches, for the later runs 10.0 inches.

accomplished by adding mercury dropwise from a 100 ml. chemical burette into a small beaker suspended from the bar by a string at the mid-point between the bearing blocks.

All tests were made at approximately the same loading rate.

The deflection of the bar was measured by the use of a micrometer telescope. During each test readings of load added (in ml. of Hg) and deflection of the bar in centimeters were recorded at one-half minute intervals up to the time at which the bar broke. Samples of clay were immediately taken for moisture determination.

Graphs were then drawn for each run. Load added in grams was plotted against deflection in centimeters. Without exception, each of these curves had a straight-line portion at the beginning of the test indicating that up to a certain point, the deflection was directly proportional to the load.

In order to obtain values of E, use was made of the formula:

$$\Delta = \frac{PL^3}{48\ EI}$$

where:

Δ = Deflection due to the concentrated load at the center of the bar.

P = Weight added at mid-point of the bar.

E = Modulus of elasticity.

I = Moment of inertia about centroidal axis parallel to the base (i.e. about the diameter of the bar).

L = Length of the beam between supports.

To calculate the value of E for each run a rearrangement is necessary to give

$$E = \frac{L^3}{48\ I}\left[\frac{P}{\Delta}\right]$$

In making the calculation the term in brackets in the preceding equation was taken as the average slope of the entire load-deflection diagram to the breaking point. This is not a true value of modulus of elasticity due to the change in slope of the load-deflection diagram. Nevertheless, it was thought to more nearly represent the conditions encountered under drying than would a modulus calculated from the straight-line portion of the load-deflection curve. In the drying specimen, the condition of the material may range all the way from that which is stressed below the proportional limit to that which has reached the ultimate stress and is beginning to rupture. Hence, a modified modulus of elasticity would seem to be necessary to make a calculation of the stresses encountered.

In these calculations, no correction was applied to compensate for the deflection caused by the uniform load of the beam, because (1) the deflection due to this weight was not measured (the zero reading for deflection was taken with that uniform weight acting on the beam), (2) the weight of the beam was small compared to the total load on the beam at the breaking point, particularly in the case of the drier specimens and (3) a modified and necessarily approximate modulus was being calculated and a closer evaluation of the effect of the small uniform weight was therefore not warranted.

D. Drying shrinkage.

For the preliminary shrinkage tests the same body was used that had been used for the drying and tensile tests. It was slaked and thoroughly mixed with distilled water to form a slip of about 1.80 specific gravity. Castings were made that were 1.2 cm. x 6.35 cm. x 11.45 cm. Normal casting time was about two hours. Shrinkage Test No. 6 was made on a specimen that was in the mold only one hour and, hence, it was wetter when the test was started than were the other specimens.

Specimens 1.2 cm. x 3 cm. x 11.4 cm. were obtained from the castings described above.

A measured distance of 4 cm.[1] was marked off on one face of the specimen by two parallel lines. In order to avoid error due to malalignment during subsequent readings, small vertical marks were made across each of the parallel lines such that the distance measured each time should be between the same two points.

The specimen was mounted vertically in the drier and was held vertical, though not rigid, by a specially prepared stand. This stand was in turn mounted on a sheet metal pan connected to a balance above it. Continuous weight readings were made from which the moisture contents and drying rates were determined.

A micrometer telescope was used for the determination of the distance between the lines on the piece. Readings were taken at frequent intervals especially during the early part of the drying operation. It was soon found that when the piece was below 10 to 12% H_2O, there was very little variation in the linear dimension until just before the specimen became dry, at which time a slight expansion was noted.

It was decided that the shrinkage data obtained by the method just outlined were not accurate enough for application to stress calculations. Accordingly, an automatic drying

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[1]Tests No. 1 and 2 were made using a measured distance of 5 cm.

shrinkage measuring machine which had been under construction by the department was rushed to completion and used to obtain the necessary data relating per cent linear shrinkage and moisture content.

The machine was patterned after a similar unit pictured and described in the literature by Norton[1]. It incorporates an optical micrometer device for measuring shrinkage and an automatic indicating motor-driven balance mechanism from which moisture contents may be computed.

The specimens dried in these tests were cylindrical shells 7/8 inch in outside diameter with a wall thickness of 1/8 inch. The specimens used had a gage length of approximately 2-2/3 inches. Drying was begun at a moisture content of approximately 22% (calculated on a dry basis) and carried to dryness.

Measurements were made for both the calcium clay and the sodium clay in order to get results which would be applicable to the clays used in the drying runs.

The per cent linear shrinkage (unit strain x 100) and moisture content were both calculated on the dry basis for all runs. Results are shown in Figures 3 and 4.

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[1]Norton, F. H., "Precise Measurement of Drying Shrinkage", Ceram. Age, 33, 7-8 (1939).

E. Particle size.

One of the important factors which affect cracking of clay in the drying operation is the particle size of the clay. Time did not permit an examination of the cracking tendencies of clays of different particle sizes. Therefore, it was decided to hold this variable constant by using a clay material from only one source. Two check runs were then made to determine the particle size distribution in the body composition employed in the other tests.

A standard procedure, as recommended by Norton and Speil[1], was employed. This method is one based on measurements of the rate of settling and calculation of particle size by the use of Stokes Law. A long-arm centrifuge was used to speed up the rate of settling for the finer particle sizes.

In the determinations made here, 12.7 gram samples of the body (dry basis) were added to 200-300 ml. of water to which was added 0.14 grams of Daxad 23 to act as a dispersing agent. The samples were placed in quart jars and tumbled end over end for 24 hours at the rate of about 60 R.P.M. The suspensions were then passed through a 325-mesh screen with the exception of about 1.3 grams (10% of the original weight)

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[1]Norton, F. H. and Speil, S., "The Measurement of Particle Sizes in Clays", Jour. Amer. Ceram. Soc., 21, 89-97 (1938).

which was too coarse. Most of this amount was considered to be flint or feldspar from the body. The suspension which passed the 325 mesh screen was transferred to 700 ml. test tubes in which the density was determined by hydrometer at regular time intervals after the settling started and until the solid particles were completely settled out leaving a clear supernatant liquid. Results were plotted as per cent finer than a given particle size against equivalent spherical diameter in microns. See the Appendix for the actual distribution (Figure 17).

F. Thermal analysis.

The type of clay mineral and the body composition used also have a direct bearing on the question of cracks due to drying. The procedure followed was one of holding this variable constant by using only one clay mineral in one body composition. A thermal analysis was made to determine the clay mineral (or minerals) present, and it was found that kaolinite was the only one in the body composition used.

The method of analysis was the same as that recommended by Norton[1] which employs two thermocouples, one imbedded in

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[1]Norton, F. H., "Critical Study of the Differential Thermal Method for Identification of the Clay Minerals", Jour. Amer. Ceram. Soc., 22, 54-63 (1939).

the sample being tested and one in a neutral reference material at the same conditions with regard to the thermal furnace. The differential temperature was read with a recording galvanometer which was arranged with three possible ranges of sensitivity. A continuous record was produced on photographic paper and is reproduced in the Appendix in Figure 16.

The sample was prepared from 600 ml. of the suspension used in the particle size determination which contained only particles finer than 0.25 micron in size. The suspension was treated with two 10 ml. portions of hydrogen peroxide in order to oxidize most of the organic matter which may have been present. The suspension was then dried in an oven at 150° to 180°F. After drying, 0.4 gram of the material was analyzed according to the method outlined by Norton.

The photographic record of the analysis was compared with curves for the pure minerals shown by Norton[1]. There are two irregularities in the graph. A small peak just above 100°C was taken to be mechanically bound water. A second exothermic peak at 710° was assumed to be organic matter burning out which had not been completely oxidized by the hydrogen peroxide treatment. Neither of these irregularities remotely resembled the curves for any of the pure clay minerals.

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[1]Ibid.

Pure kaolinite was shown by Norton to exhibit an endothermic peak at 610°C and an exothermic peak at 980°C. These two characteristics are evident in Figure 16. It was concluded that kaolinite was the only clay mineral present in an amount large enough to be significant.

IV. RESULTS AND DISCUSSION

A. Drying tests.

The most important results obtained from these tests were those showing the moisture gradient at the time the cracks were developed. Drying rate curves were also obtained.

Table I shows some selected results for both calcium clay and sodium clay samples for tests which showed cracks and tests which did not.

It can be seen by comparison of the data for the different runs listed in Table I that the magnitude of the moisture gradients is not the whole key to the cracking problem. Note that the gradient in Run 37 is much higher than that for any of the other runs listed for sodium clay and yet this sample did not crack. It may be noted that though the samples of each of the other four runs on sodium clay did crack, the moisture gradients were not constant as might have been expected but increased in the order listed. There are two contributing factors which may be used to explain this feature of the data. It may be seen that for the runs just mentioned in which the moisture gradients increased, there was a corresponding decrease in surface moisture contents at the time of cracking. This caused decreasing values of unit strain (with the exception of Run 20 which may be inaccurate

Table I

Run No.	Initial Moisture	Moisture Gradient M - Ms	Surface Moisture Ms	Unit Strain	Time of Drying	Drying[1] Rate	Drying[2] Rate	Remarks
	%	%	%	in./in.	min.	g/cm^2-hr.		
Drying test results								
Sodium Clay								
18	19.56	5.77	7.80	0.00086	24	0.366	0.326	Cracked
20	20.30	7.06	7.69	0.00249	23	0.366	0.333	Cracked
35	20.60	7.48	5.34	0.00045	20.5	0.441	0.390	Cracked
34	20.90	7.89	4.91	0.00045	28	0.375	0.322	Cracked
37	22.03	9.12	3.98	0.00035	30.5	0.397	0.332	No crack
Calcium Clay								
40	22.15	4.12	8.63	0.0006	37		0.216	No crack
39	21.39	7.36	7.34	0.0024	22		0.354	Cracked
38	22.35	7.51	6.50	0.0016	27		0.334	Cracked

[1]Constant rate period only.

[2]Average drying rate until run was interrupted.

for some other reason), because more of the material had already reached its shrinkage limit. The decreasing values for surface moisture contents also mean that progressively higher moduli of elasticity are applicable (see Figure 5). Hence, the maximum tensile stress developed on the surface would logically be expected to be nearly the same for these four

runs since that stress is a function of the product of modulus of elasticity and unit strain. The decreasing values of unit strain are thus compensated for by increasing values of modulus of elasticity.

Although fewer runs were made for the calcium clay, the same explanations seem to apply to those runs that were made.

Another interesting feature of the data in the table is the fact that, in general, the longer the drying time the greater the moisture gradient indicating that the moisture gradients had apparently not reached their peaks at the time the cracks occurred. (In Run 35 this generalization does not hold, but it was noted that the drying rate was somewhat greater for this run thus accounting for the combination of high gradient and short drying time.) This fact may be utilized in explaining one apparent inconsistency in the data. For instance, if the moisture gradient in Run 37 had been at the value 9.12% for some time during the run, the sample could not possibly have passed through the critical period just prior to the end of surface shrinkage without becoming cracked. The only explanation to be offered is that the moisture gradient existing when the sample was in the critical moisture range must have been considerably lower than the 9.12% measured when the run was interrupted.

The drying rate for Run 40 was much less than the other

two runs on the calcium clay thus accounting for the lower moisture gradient and the fact that the sample did not crack.

Sample calculations for some of the items listed in Table I are given in the Appendix.

B. Tensile tests.

In giving the procedure followed for the tensile tests, reference was made to the fact that a correction factor was necessary in the calculation of ultimate tensile strength in order to compensate for the stress concentration caused by the shape of the briquet. The authority for this statement is an article by Coker and Filon[1]. Photo-elastic studies were made of the type of briquet specimen used in these tensile tests, and it was found that the maximum tensile stress existing in the cross-section of the briquet just prior to breaking was 1.74 times the value of the mean stress and occurred along the edges of the broken cross-section. The minimum value was indicated as 80% of the mean average value and occurred at the center of the broken cross-section.

The fact that the clay used in these tests was not perfectly elastic would render these results not completely

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[1]Coker, E. G. and Filon, L. N. G., "A Treatise on Photo-Elasticity", p. 578-83, Cambridge, England, The University Press, 1931.

applicable, just as Coker and Filon indicated for tests on freshly moulded cement. They stated that (p. 582)

> . . . the freshly moulded cement briquettes are most probably in a semi-elastic condition in which, as all evidence we possess indicates, the stress distribution is less variable than in the purely elastic state, so that any provisions found necessary from experiments on elastic bodies will more than cover the requirements sought.

These observations should apply to the clay specimens as well, indicating that the true value of the maximum tensile stress for the inelastic clay would be somewhere between the (P/A) value and the value of 1.74 (P/A).

The value of 1.74 (P/A) was the one calculated and plotted for the various moisture contents in Figure 2. It was noted that there was considerable scattering of experimental points on this figure, but that only serves to point out the well known fact that it is extremely difficult to turn out two clay samples even from the same batch, that have identical properties. As pointed out in the tensile test procedure, this scattering was probably due to air holes or other faults in the specimens, or to an eccentric loading condition in the testing machine. No attempt was made to measure the strain on opposite sides of the briquet or to re-align the grips to eliminate eccentric loading.

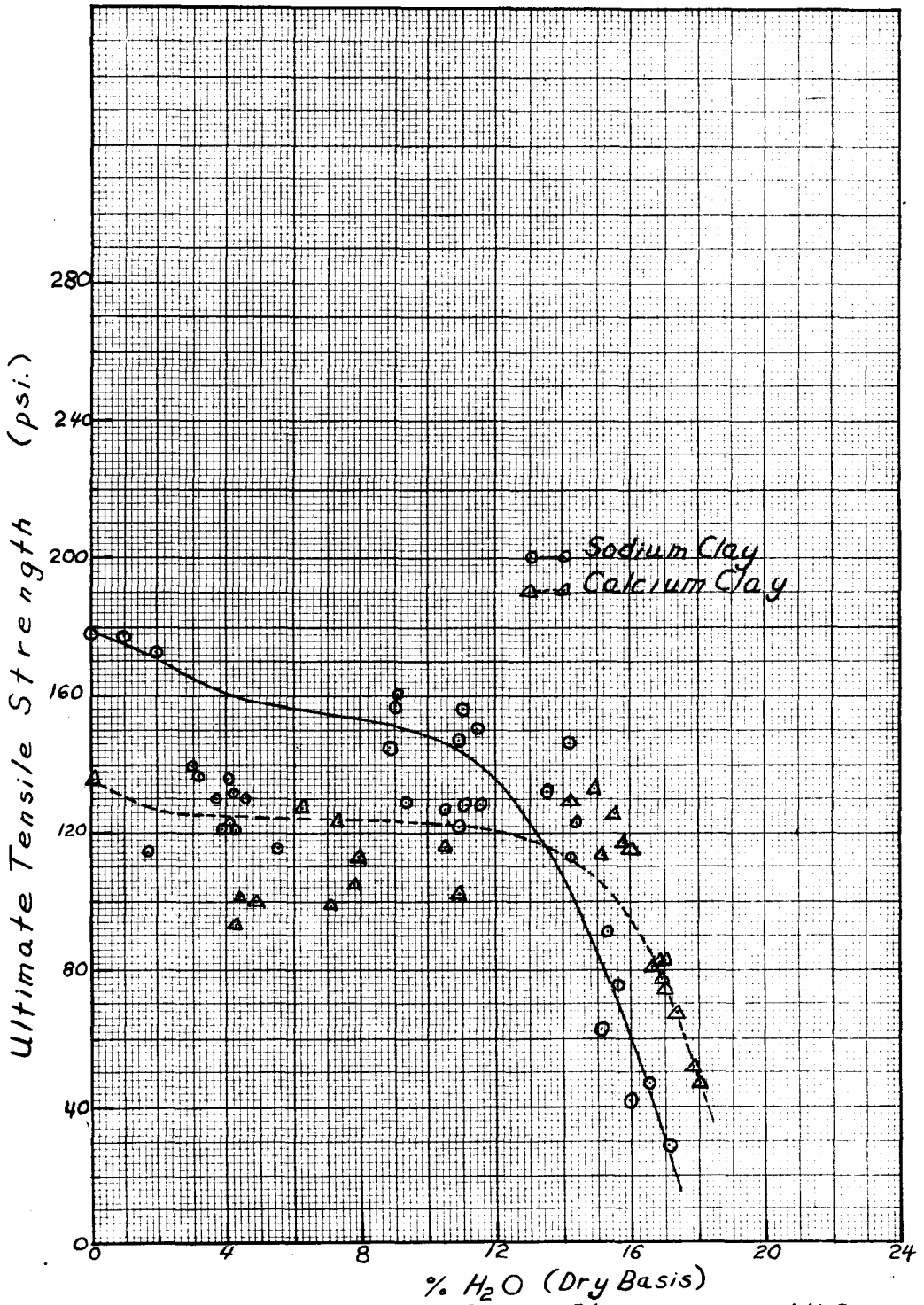

Figure 2. Ultimate Tensile Strength vs. % H_2O

It was recommended by Coker and Filon[1] that a modified shape of briquet be used in order to eliminate most of the effect of the stress concentration discussed here. The modified shape would be essentially the same as the standard one now in use with the exception that it would include a section in the center with straight sides of a predetermined length. Then if the sample ruptured within the straight-edged portion, the value of (P/A) could be considered as pure tensile stress.

It is believed that a modified briquet of this type would have aided in this work in making the ultimate tensile strength results more consistent.

As far as the knowledge of the author is concerned, no material has yet been published showing ultimate tensile strength of clay as a function of moisture content. Dry strength and fired strength data have been published for a number of different clays. No information seems to be available on the exact type of function relating wet tensile strength and per cent H_2O over the moisture range encountered in drying.

As early as 1918, Saxe and Buckner[2] reported dry tensile strengths for several different clays that had been

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[1] Ibid.

[2] Saxe, C. W. and Buckner, O. S., "The Bonding Strengths of a Number of Clays Between Normal Temperature and Red Heat", Jour. Amer. Ceram. Soc., 1, 113-33 (1918).

dried at different temperatures. They also determined the effect of high temperatures at the time of the tensile test on breaking strength. No attempt was made by these men to correlate moisture content and ultimate tensile strength. However, they did observe that clay briquets, whether dried in air at room temperature or at 110°C showed a tendency to become weaker if allowed to stand and take up water in a moist atmosphere before being tested. These observations are substantiated by the present work in which a fairly sharp increase in strength is noted for a small decrease in moisture content near dryness.

It is believed to be significant that the clay increases in strength in a direct proportion to the decrease in moisture content down to the range in which the shrinkage limit for the clay is reached. Beyond this point little or no increase in strength is noted until just before complete dryness is reached at which time a rather sharp jump in ultimate tensile strength was recorded. Results of further tests with more consistent data should be available, however, before any definite conclusions are offered concerning this behavior.

C. Drying shrinkage.

In each of the graphs on the following pages of per cent linear shrinkage as a function of moisture content, the portion of the curve in the very wet region (i.e. from the

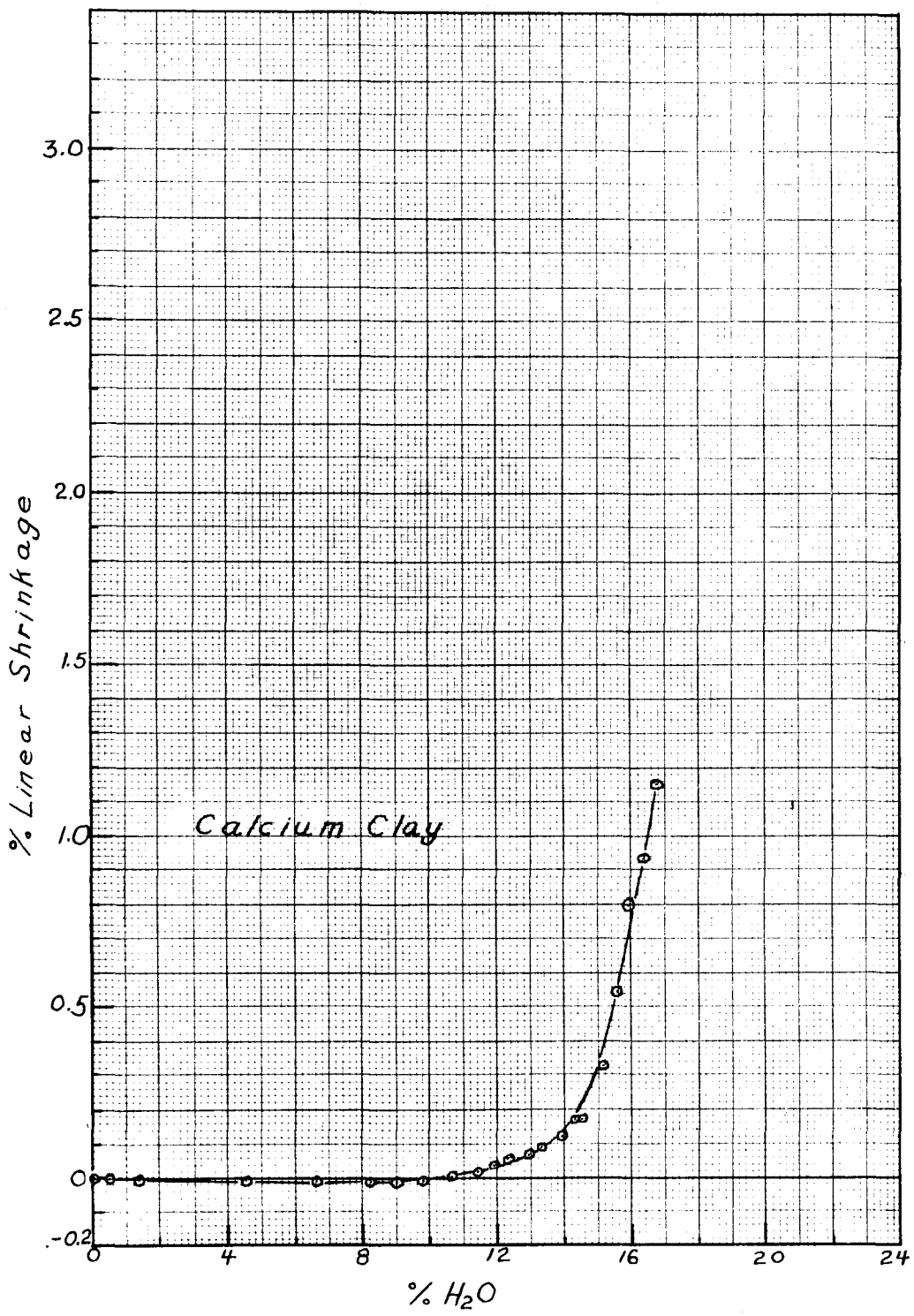

Figure 3. % Linear Shrinkage vs. % H_2O (Dry Basis)

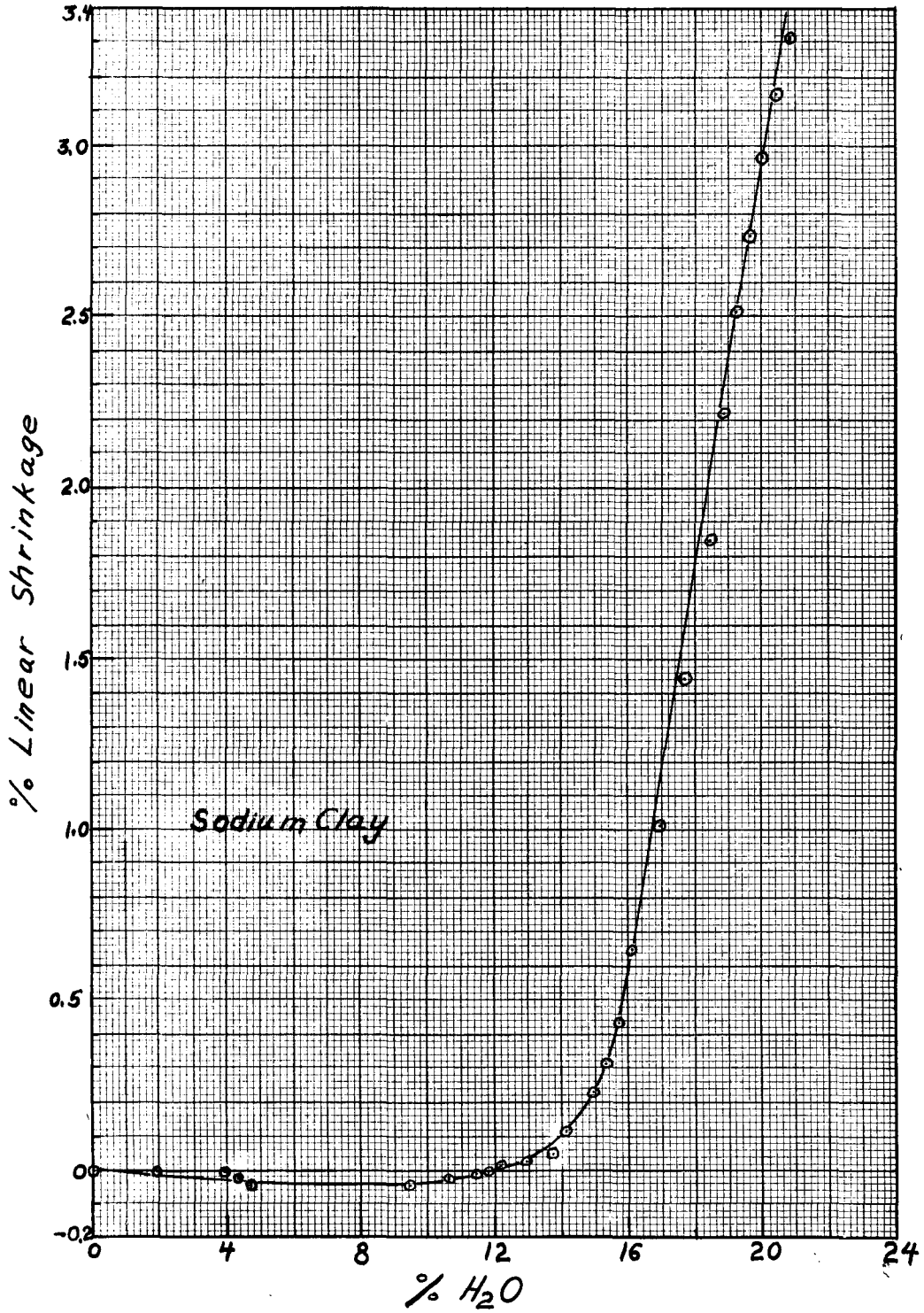

Figure 4. % Linear Shrinkage vs. % H_2O (Dry Basis)

initial moisture content down to about 15% H_2O) is very nearly a straight line. This indicates that the shrinkage is directly proportional to the amount of water removed. This fact has been reported by several other investigators.[1]

The point at which the curves first reach zero per cent shrinkage is that moisture content referred to as the shrinkage limit. This limit is 11% H_2O for the calcium clay and 12% H_2O for the sodium clay. Beyond this point in the drying operation, the dimensions of the drying body tend to drop slightly below their final values and remain there until just before complete dryness is reached when a slight expansion is noted. This behavior has likewise been reported before for kaolinite.[1] A completely satisfactory explanation has not yet been offered, but at least two theories have been mentioned.

One of the explanations for the expansion just prior to the dry condition is based upon thermal expansion of the clay assuming that as evaporation ceases, the surface temperature rises from the wet-bulb temperature to the dry-bulb temperature of the air stream thus causing the body to increase in size.

A second explanation is based on the theory that the

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[1]Norton, F. H., "Refractories", 2d ed., p. 266-71, New York, McGraw-Hill Book Company, Inc., 1942.

suction pressure within the capillary network in the clay is greater after part of the voids between particles have been emptied of water. This increase of suction tends to draw the clay particles closer together than they are when no water is present as at complete dryness.

No attempt is made here to point to either of the above theories as the correct one for the behavior noted. Further experimentation will be necessary to completely explain this phenomenon.

D. Modulus of elasticity.

The modulus of elasticity of this body was found to be a definite function of moisture content as shown by Figure 5. It was found that the curve for the sodium clay assumed the form of a hyperbola from 18% down to 8% H_2O. Below this water content, the curve deviated somewhat from the hyperbolic path, but since this includes most of the range which is considered to be critical, the assumption may be made that

$$E = E_1 - \frac{M-M_1}{mM - b}$$

where E = modulus of elasticity of any point at a moisture content M.

E_1 = modulus of elasticity at a particular point at the moisture content M_1.

m = slope of the rectified plot of the term $\frac{M-M_1}{E_1-E}$ as a function of M.

b = the ordinate intercept on the rectified plot.

The procedure for rectification of data of this type to obtain a straight-line plot was outlined by Davis[1]. Table II shows the data and calculated results necessary to convert the original graph of E versus M into a straight-line graph. After the straight-line plot is obtained, it is a simple matter to write the equation of it by standard methods.

A plot for the calcium clay similar to that shown in Figure 6 for the sodium clay was not as satisfactory, but this was probably due to data which were inaccurate for one reason or another. More flexural tests were run for the calcium clay than for the sodium clay, but in spite of this there was less indication of the true relationship between E and M due to a scattering of the experimental points as shown in Figure 5.

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[1]Davis, D. S., "Empirical Equations and Nomography", p. 24-6, New York, McGraw-Hill Book Company, Inc., 1943.

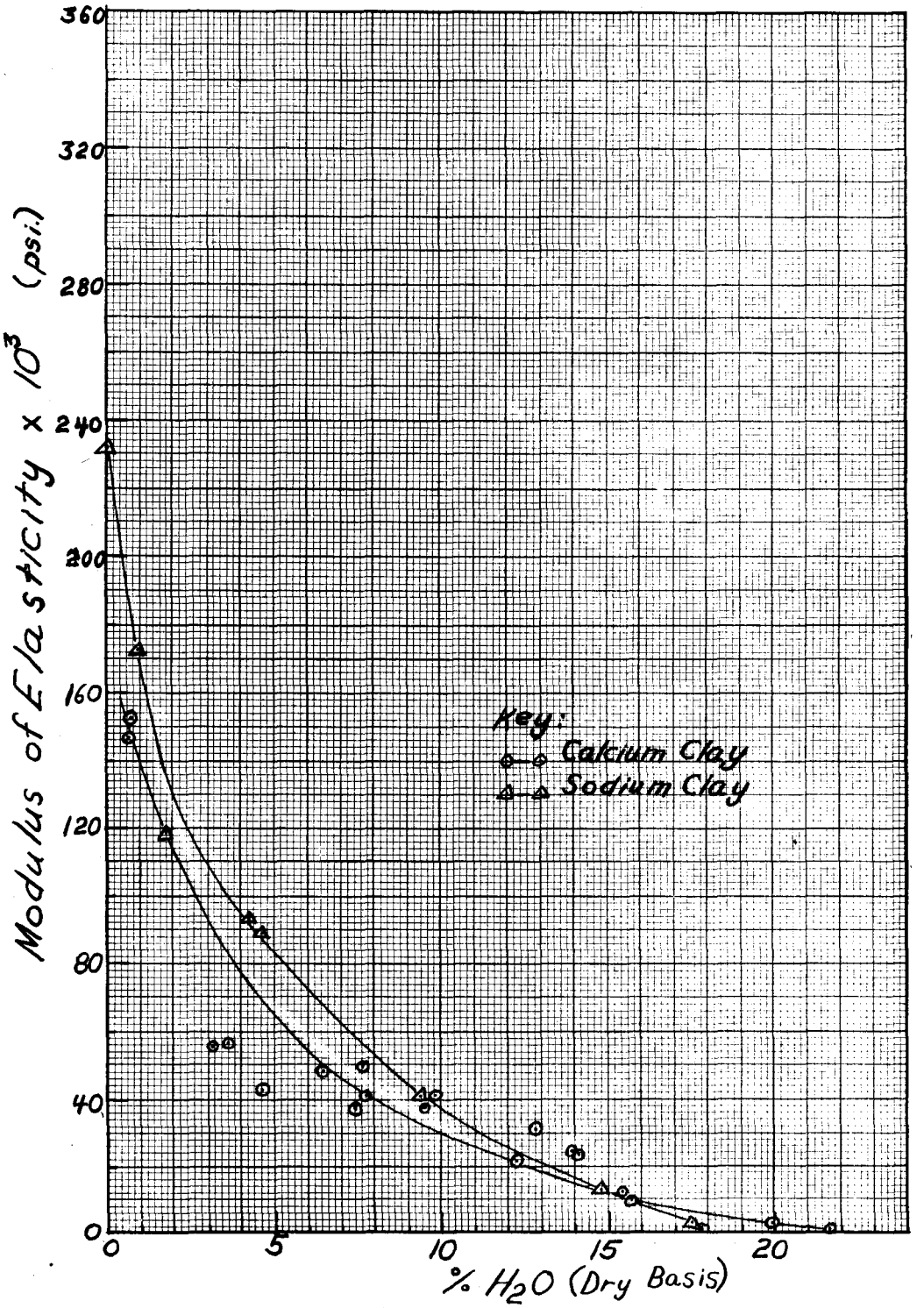


Figure 5. Modulus of Elasticity vs. % H_2O

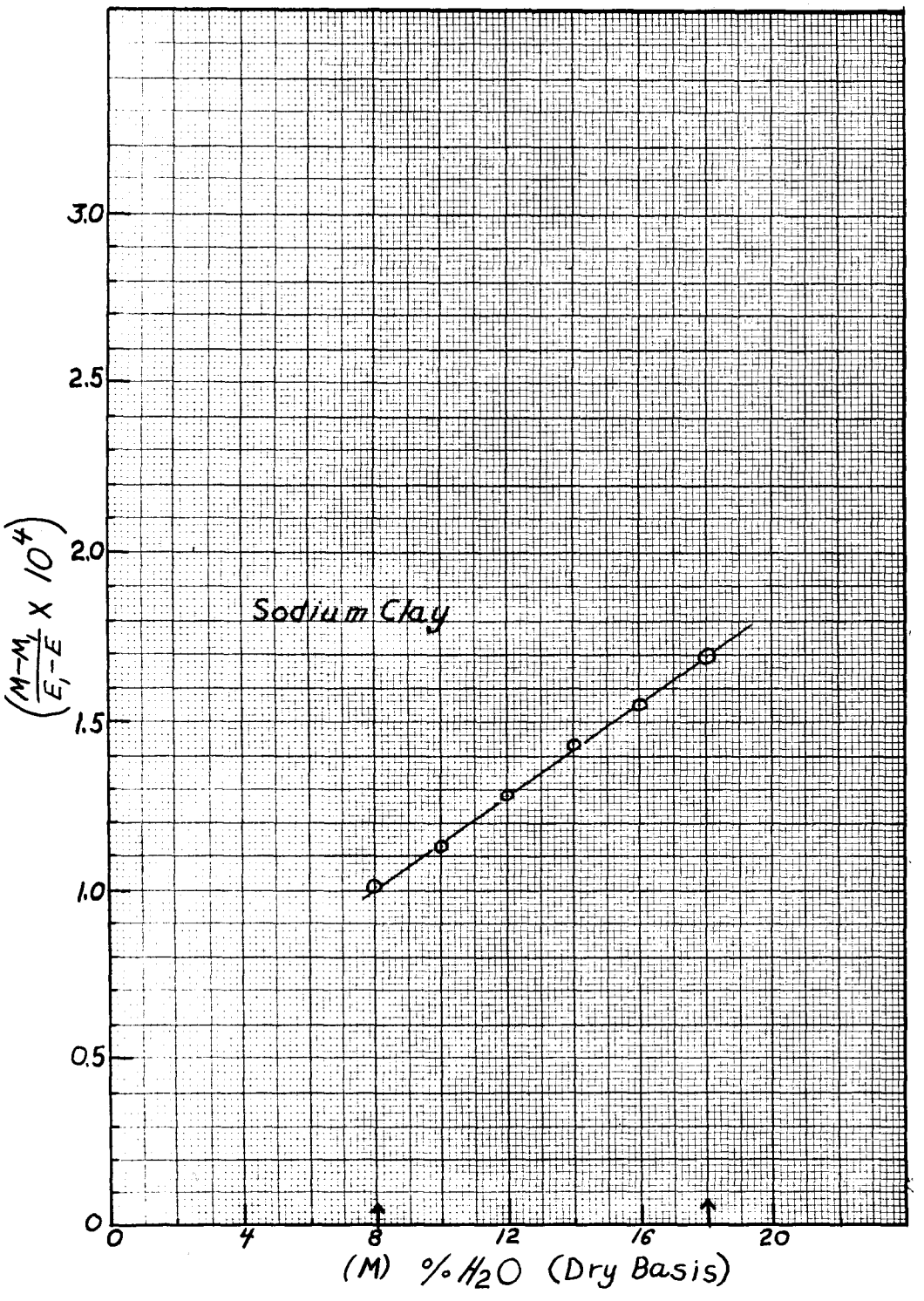


Figure 6. Modulus of Elasticity vs. % H_2O (Modified)

Table II

Rectification of data to produce a straight-line function of modulus of elasticity and moisture content.

M %	E psi	$(M-M_1)$	(E_1-E)	$\frac{M-M_1}{E_1-E} \times 10^4$
$M_1 = 6$	$E_1 = 72,800$	0	0	---
8	53,000	2	19,800	1.010
10	37,200	4	35,600	1.124
12	26,000	6	46,800	1.281
14	17,000	8	55,800	1.433
16	8,300	10	64,500	1.550
18	2,000	12	70,800	1.695

This work has shown qualitatively that there is a definite relationship between modulus of elasticity and moisture content, and has shown what that relationship is for one particular body composition within the critical range of moisture for the drying operation. However, work should be done on a large number of different clays and these data evaluated in a manner similar to that done here before a positive general statement may be made regarding the interrelation of the two variables. This is one of the more important parts of the foundation needed before a rigorous stress analysis for drying clayware may be completed.

E. General.

In the drying runs conducted in this work, the type of specimen selected was a two-inch cube of wet clay. After the drying operation has proceeded for some time, the contour lines for moisture content may be imagined to be as shown below. The diagram is intended to represent a cross-section through the center of the cube just before the cracks appeared. The material at the center of the cube is at a higher moisture content than the clay material on the outside surfaces.

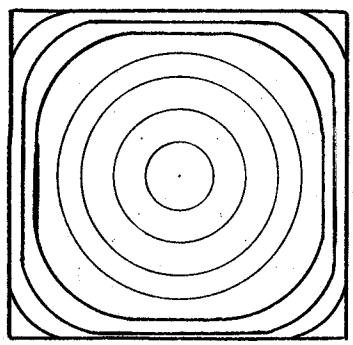


Figure 7. Cross-section view of cube showing per cent moisture contours.

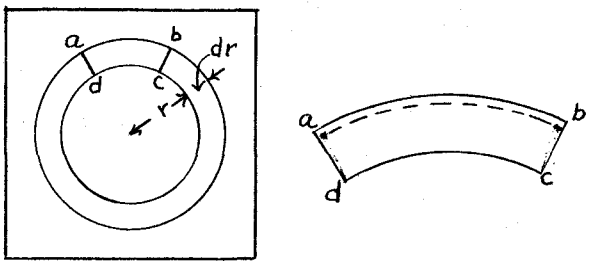
Since the corners and edges of the cube are being dried from more than one surface they will tend to become drier than the flat sides. Proceeding from the outer surface toward the center of the cube the contour lines for moisture content become nearly spherical in shape. This is an approximation for an actual case, but theoretically it would be

true if the drying were carried out slowly and under fairly constant conditions.

In addition to the water content being constant on any spherical segment as stated above, the total shrinkage which any two points on that segment have undergone with respect to their original condition is the same.

If the premise is made that stresses at a point in the body are due to a difference in shrinkage between that point and the center of the body, then the stresses must also be the same at any two points in one of the spherical segments. Therefore, the spherical segments shown on Figure 7 are contour lines for moisture content, drying shrinkage and stress.

If a short section of a spherical shell of thickness (dr) is examined in cross-section as shown in Figure 8-b, it can be seen that the shrinkage during drying will cause it to take on the appearance shown by the dotted lines in Figure 8-b. The surface $\overline{ab}$ is drier than the surface $\overline{dc}$ and thus has shrunk more than has $\overline{dc}$.



Heavy lines indicate the original dimensions when the entire body was at the same moisture content.

Dotted lines show dimensions after the specimen is partially dried.

(a) (b)

Figure 8. Effect of shrinkage during drying.

When it is remembered that the section $\overline{abcda}$ is part of a spherical shell and that it is the outside surface of this shell which is shrinking the fastest, it is easily seen that the wet interior of the sphere must be compressed or else the drier shell will break if its ultimate tensile strength is exceeded.

As the outer shell shrinks, the situation becomes analogous to that existing when a spherical vessel is subjected to an internal gas or liquid pressure. In this case, the wet clay on the interior of the sphere is relatively incompressible thus resisting any shrinkage of the outer shell. If the shrinkage becomes too great, the shell will burst just as a toy balloon does when inflated with too much air. Referring to the following figure, it can be seen that a tensile stress will be set up in the thin spherical shell due to the internal pressure, if that pressure is greater than the external radial pressure.[1]

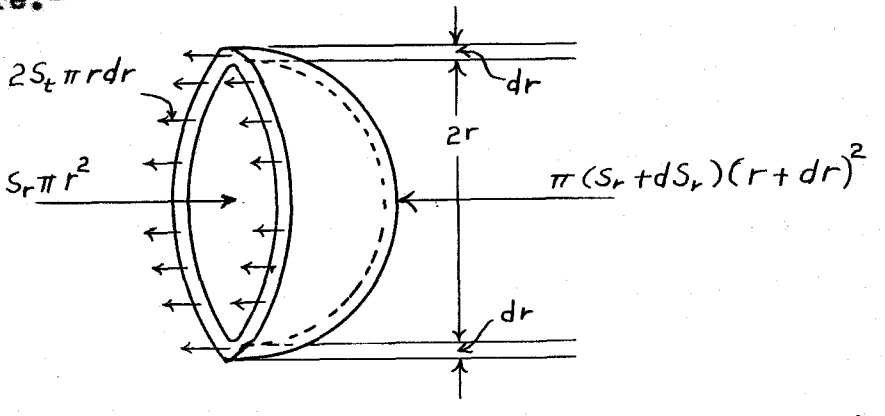


Figure 9. Equilibrium of stresses in a spherical shell.

[1]See the Appendix for a further discussion of the development of tangential stress equations.

Where:

S_t = tensile unit stress acting on the walls of the sphere in a tangential direction.

S_r = resultant internal pressure due to shrinkage, (radial stress).

r = radius of spherical shell.

dr = thickness of shell.

$(S_r + dS_r)$ = resultant external pressure due to shrinkage, (radial stress).

If the tensile stress caused by the drying shrinkage exceeds the ultimate tensile strength of the clay at that moisture content, a crack is developed. As soon as a crack is formed, the stress distribution is altered so that it is no longer as pictured in Figure 7 but becomes much more complex. It is known that the unit stress is generally intensified in the region nearest a sharp corner or crack in any material under stress. Therefore, it is believed that this factor contributes to enlargement of the crack in the clay until eventually it may be visually observed on the surface of the specimen even though it may have been so small as to be invisible to the naked eye when first formed.

The shell in Figure 8 was picked at random anywhere in the cube so that what has just been said about the point at which a crack first forms applies equally well to any point

or points within the cube. There are, however, limitations on the position where a crack may be formed which need to be discussed. Since wet clay is a plastic material, there is a certain range of moisture content (i.e. very wet clay) within which the clay simply deforms without breaking. The exact lower limit of this moisture range is not known for the present conditions. Certainly when the clay becomes dry enough to act as an elastic material, it may be considered to be outside the plastic range. It is probable that there is a gradual transition between the two conditions. This point is mentioned in connection with an effort to predict where the cracks first develop with regard to moisture content. The lower limit (in moisture content) of the plastic range thus forms the upper limit of the range in which a crack could be caused by exceeding the ultimate tensile strength of the clay.

There is also a lower limit of the range just mentioned, and that limit is the moisture content of the clay at which drying shrinkage ceases. For the present clay this was approximately 11 to 12% water (dry basis). Below this limit, cracks are unlikely to form. If the entire clay piece is at the same level as far as shrinkage is concerned, it would also be at the same level with regard to stress because the stresses are believed to be set up originally by a difference in the shrinkage that has taken place between the surface and

the interior of the body. This is true, however, only when the entire clay piece has reached the shrinkage limit.

The critical period in drying occurs when the surface has reached the leather-hard stage characteristic of clay at a moisture content very near the shrinkage limit. It is believed by this writer that this is the most critical section of the drying operation, because stresses are likely to be at a maximum at or near the time the surface reaches its final dimensions.

F. Thermal stress analogy.

In support of the conclusion that the most critical drying period is in the moisture range at the shrinkage limit, use is made of an analogy with thermal stresses developed when the surface of a hot, solid sphere is suddenly cooled by plunging it into a cold liquid bath. The theoretical stress relations for a solid steel sphere under these conditions have been presented by Kent[1].

In summarizing, Kent made the statement:

> It is noticed that the maximum tensile stresses of both bodies [spheres and cylinders] occur at the surface

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[1]Kent, C. H., "Thermal Stresses in Spheres and Cylinders Produced by Temperatures Varying With Time", Trans. Amer. Soc. of Mech. Engrs., 54, Paper APM-54-18, 185-196 (1932).

at the beginning of the cooling, and that these values are equal in the two cases and are given by $\left(\frac{EaT_1}{1-\mu}\right)$

where T_1 is the temperature change of the surface, a is the linear coefficient of thermal expansion, and E and μ are the elastic constants. This is seen to be independent of the shape and size of the body and to depend only on the temperature change and the properties of the material. It is equivalent to the stress produced in a thin plate when its temperature is changed T_1 degrees and a change in area is prevented. The very thin layer of the external surface of a body of any shape or size, whose temperature is affected by a sudden change, is prevented from changing its area by the relatively very large mass of the rest of the body. As the time curves show, this stress is only momentary and rapidly drops as the reduction of temperature spreads inward and a contraction of the outside layer is permitted.

In the drying problem under discussion, the moisture gradient takes the place of the temperature gradient which was the controlling factor in Kent's thermal stress analysis. In the drying operation, however, the tensile stress at the surface increases as a function of time from the beginning of the drying run until the unit strain caused by shrinkage reaches its highest value. As the unit strain drops off when the surface moisture content passes the shrinkage limit, the surface tensile stress also decreases. If the moisture gradient is such that the stresses in the piece remain below the allowable stress until dryness is reached, no cracks will be developed. The stress values will have gone from zero at the beginning of the run through a maximum when the factors of moisture gradient, modulus of elasticity and shrinkage combine to give optimum conditions for a highly stressed

material, and then will again fall to zero at the time the center of the piece reaches its shrinkage limit.

One important and complicating difference between the drying clay sphere and the cooling steel sphere is the fact that the modulus of elasticity, while essentially constant over a reasonable temperature range for steel, is definitely not a constant over the moisture range considered for the clay. The modulus of elasticity for the calcium clay and for the sodium clay has been shown as a function of moisture content in Figure 5. As shown by the figure, the moduli increase quite rapidly with decrease of moisture content, particularly in the drier range. This means that if the amount of strain existing between the center and the surface of a body were to remain constant during a part of the drying operation, the stress exerted on the material would be continually increasing due to the increase in modulus of elasticity alone. This generalization may be made even though the exact mathematical relation is not known for the triaxial stress-strain conditions encountered here.

It was shown by Kent[1] that the stress distribution for the cooling sphere as previously discussed was as shown in Figure 10.

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[1]Ibid.

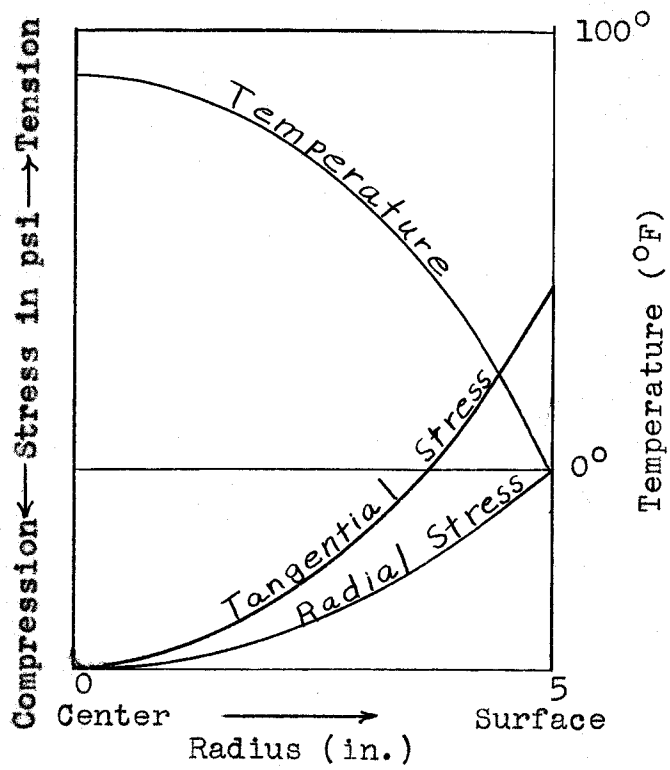

Figure 10. Temperature and stress distribution in solid steel sphere 5 inches in diameter, one minute after surface is cooled 100°F below the original temperature.

The maximum tensile stress shown to occur on the surface of the sphere at the instant it was plunged into its cooling bath was equal to $\left(\frac{EaT_1}{1-\mu}\right)$ in which tensile stress is directly proportional to the product of modulus of elasticity (E), and the thermal contraction (aT_1). In the drying of a clay sphere a similar expression would be expected to be applicable except that E would have to be replaced by some function of moisture content such that E would increase as the per cent moisture in the clay decreased. For a particular instant in

the drying operation, say the time at which a crack was first formed, E could be expressed as a function of the sphere radius if the moisture gradient were known. Obviously, the value of the stress at the surface must increase during the drying run as long as the moisture gradient, and therefore differential shrinkage between surface and center of the sphere, is increasing or remains at a constant value. As the unit strain caused by the moisture gradient tends to drop off, a point will be reached at which the tangential stress will drop off in spite of an increasing modulus of elasticity.

G. Graphical interpretation.

This theory may be more easily followed by observing the following figures.

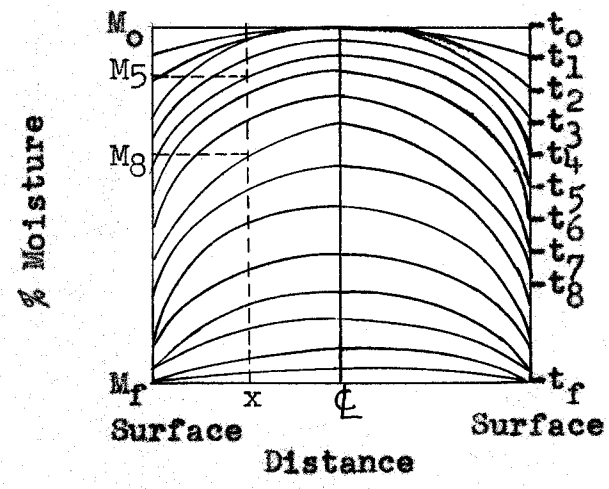

Figure 11. Moisture distribution as a function of time and distance from the drying surface.

The diagram above represents a line through the center of the drying cube, sphere or other shape with the curves labelled t_o, t_1, t_2 etc. being the moisture gradient in the cube at successive stages of drying. The entire cube is at a moisture content M_o at the time t_o. As drying progresses the moisture content at any point (x) on the line through the center of the cube is represented by the value M_5 shown on the left margin at the time t_5, and for the same point by the value M_8 at the time t_8.

It may be seen from the preceding figure that the moisture gradient (meaning the over-all moisture content difference from surface to center line) is zero at the time t_o when drying is started, increases throughout most of the run until a peak value is obtained, and then drops off to zero as dryness is reached. This may also be expressed as is done by curve (1) in Figure 12.

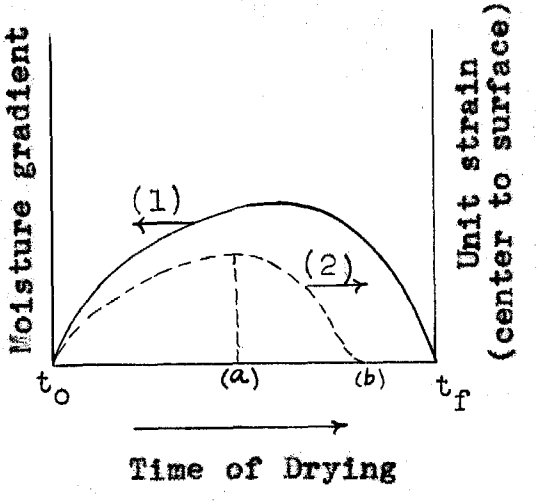

Figure 12. Moisture gradient and unit strain as functions of the cumulative time of drying.

Curve (2) in Figure 12 for unit strain as a function of the time of drying is somewhat similar to the moisture gradient except that it tends to drop off to zero sooner. This is to be expected because the unit strain (or differential shrinkage between the surface and the center of the body) is essentially a straight line function of moisture content in the wetter range (down to approximately 15% H_2O for this clay --see Figures 3 and 4). The unit strain, as defined above, starts to decrease as soon as the surface of the clay has reached its shrinkage limit indicated by point (a) in Figure 12. The unit strain should theoretically be zero as soon as the center of the body reaches its shrinkage limit indicated by point (b) in Figure 12. There may actually be small residual strains, and therefore stresses, still present in the material when it is completely dry due to non-homogeneity, abnormal drying conditions etc., but the magnitude of such strains would normally be small.

Since the modulus of elasticity and the unit strain are the controlling factors in determining the magnitude of the maximum tangential stress, a plot of these two items as functions of time of drying should be useful. This is done in diagrammatic form in Figure 13.

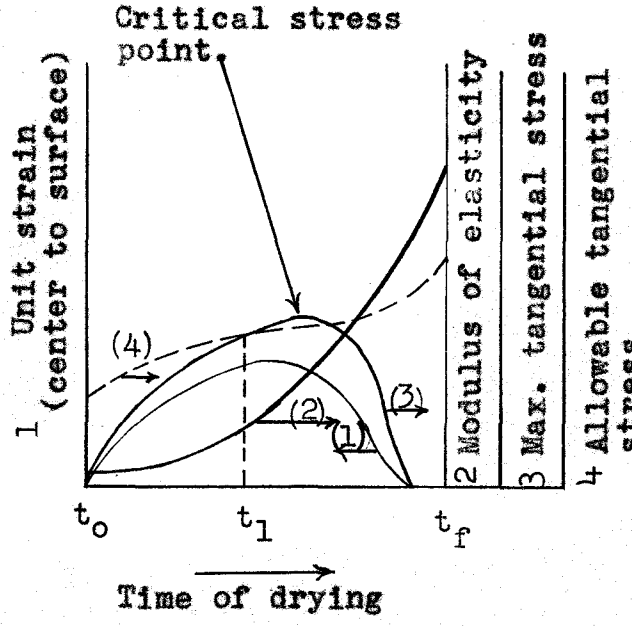

Figure 13. Unit strain, modulus of elasticity and maximum and allowable tangential stresses as functions of the cumulative time of drying.

Figure 13 illustrates the results of this project in a qualitative manner. The maximum tangential stress is primarily a function of the product of the modulus of elasticity and the unit strain. That stress when plotted as a function of the time of drying must follow a pattern similar to the solid curve (3) shown in Figure 13. A maximum occurs at or after the time at which the unit strain begins to decrease. When the effect of the decrease of unit strain on the product mentioned is greater than the effect of the increase in modulus of elasticity, the tangential stresses in the body will decrease. In order to determine the exact time at which the

maximum stress would occur on the surface, it would be necessary to have some method of making a continuous record of moisture gradients from the beginning of the drying run. The surface moisture contents and the unit strain could then be correlated with the modulus of elasticity and time of drying. A plot similar to Figure 13 could be made using the average free moisture content as the independent variable in place of the time of drying, if desired.

It is believed that the method suggested above for determination of maximum stress would probably be too tedious for ordinary practical use, even if a method of obtaining continuous moisture gradients and a rigorous method of stress calculation were available. However, the theory is logical and definitely indicates that the critical stress period in the drying of a piece of clayware is that period in which the surface shrinkage limit is reached.

Even though the maximum tensile stress is not built up until the surface shrinkage limit has been reached the piece may crack in the earlier stages of drying if too high a rate of drying is attempted. This would mean that the moisture gradient, and hence the unit strain, was large enough to cause a stress greater than the ultimate tensile strength of the material before the maximum stress conditions had been reached. Therefore, to complete the graphical illustration, curve (4) must be added to the diagram in Figure 13 showing

the allowable tensile strength as a function of drying time. Hence, if conditions for a particular drying rate were as shown in Figure 13, the surface should develop a crack at the time t_1 or very soon thereafter. If, however, curve (3) should fall below curve (4) throughout the drying run, the piece should be free from cracks when completely dry. Data for curve (4) would have to be obtained from tensile tests over a range of moisture content as was done in this project.

V. RECOMMENDED DRYING PROCEDURE

As a direct result of the observations in this investigation and the conclusions which have been drawn from them, it is possible to recommend changes in the accepted procedure for the drying of clayware.

The procedure used at present for bricks and small shapes is described by Norton[1].

> The more modern type of drier is the continuous-tunnel type, in which the load cars are pushed at a uniform rate through a tunnel having carefully regulated temperature and humidity values at each section. . . . . Usually recirculation is used; i.e., the air is passed around a closed circuit, the only vent being a small escape pipe at the top of the tunnel to allow the moisture from the bricks to pass off. The tunnel is divided longitudinally into sections, and each section is controlled for temperature and humidity by automatic controllers. In general, the temperature and humidity are high at the start to heat the brick with little loss of water from the surface. The humidity is then gradually decreased as the bricks pass through the tunnel. The regulation, however, must be determined for the particular kind of clay being dried.

Although not specified in the preceding quotation, the normal practice is to cause the airstream to flow countercurrent to the stream of clayware. One of the most common troubles encountered in this process is that of water condensation on the cold bricks or other clayware as they come

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[1]Norton, F. H., "Refractories", 2d ed., p. 277-8, New York, McGraw-Hill Book Company, Inc., 1942.

in contact with the hot, humid air at the drier entrance. The ware becomes damaged if much water condenses on it. In addition, this condensed water must be removed from the piece in the drying operation.

As a result of this investigation, the author is led to believe that the time for the drying operation may be safely shortened by use of the procedure suggested below. Also, the condensation difficulties just discussed may be greatly reduced.

It was shown in the preceding section that drying stresses are low during the first stage of the drying operation (i.e. that portion of the run from the time the ware enters the drier until the surface ceases to shrink). It was also established that the most critical portion of the drying run is that in which the surface moisture content approaches and passes the shrinkage limit.[1]

On the basis of these facts, it is recommended that a rate of drying higher than normal be obtained in the initial portion of the run by using air at a high temperature and a low humidity. As the critical period is approached, the temperature should be maintained at or near its initial level

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[1]The shrinkage limit has been defined as the moisture content of the material below which a further loss of water causes no shrinkage, and above which, addition of water causes an expansion.

and the humidity increased. When the body has passed the critical range of moisture content, the humidity should then be lowered to allow the drying to proceed as rapidly as the other practical considerations permit.

The procedure suggested requires a deliberate reduction in the drying rate during the critical period (i.e. a reduction from the rate established in the initial period in the proposed procedure). This rate would still be as high during the critical period as is allowed in present practice, and a saving in time in the initial period would already have been accomplished.

To put this plan into operation commercially, control tests would have to be run for the particular clay body and shape being used. It is recommended that the question of the time for beginning and ending the high humidity drying period be answered by use of the average free moisture content (F). The humidity should be increased when F is 4 to 5% above the shrinkage limit and decreased again when F has reached that limit. The automatic controllers for temperature and humidity already in use could be utilized in the tunnel driers. A slightly different plan of circulation for the air would probably be necessary. Since recirculation of the air is a common practice, it should not be difficult to adjust to the proposed conditions.

The use of less humid air in the section of the drier where the wet, cold ware enters should greatly reduce the condensation troubles. This advantage plus the time saved in the initial portion of the run are adequate justification for trials of the proposed method.

VI. CONCLUSIONS

Experiments were conducted in drying clayware to determine the factors which are significant in setting up stresses which cause cracking in the drying bodies. The relative importance of the different factors and the manner in which they are interrelated has been shown. As a result of this work the following facts have been established.

1. The magnitude of the moisture gradient from the drying surface to the wet interior of the clay is very significant in the range of moisture content above the shrinkage limit of the clay but loses its importance as soon as the wetter regions of the clayware have been dried below this limit. The explanation of this phenomena is that the ware, having been dried below the shrinkage limit, no longer has any but residual strains present, and these are usually insufficient to cause cracking.

2. It has been shown why the most critical period of the drying run with regard to stresses which may cause cracking occurs when the surface moisture content is approaching or has reached its shrinkage limit.

3. The modulus of elasticity of the clays tested was found to increase with a decrease of moisture content. In the range from 8 to 18% water, E was found to be a hyperbolic

function of moisture content. It is recommended that the relationship between modulus of elasticity and moisture content be established for a number of different clays in some manner similar to that outlined in this work before a rigorous theoretical stress analysis is attempted.

Qualitative results shown in this work indicate the necessity for refinements in the method of determining a usable modulus for a material such as wet clay which is only partially elastic.

4. The ultimate tensile strength is a function of moisture content, and this relationship must also be known for any particular material before a prediction can be made as to whether the clayware will fail or not for a given set of drying conditions.

5. The application of Tygon paint or other similar coating to certain portions of intricate clayware shapes in order to alter the stress distribution as an aid in reducing cracking has definite possibilities of success and should be investigated further.

6. The problem of calculation of the theoretical tangential stress developed in drying of clay bodies is an estremely complex one due to the many variables involved and the manner in which they are interdependent. The continual

variation of moisture gradient during the drying operation, particularly for high drying rates, and the variation of the modulus of elasticity with moisture content are chiefly responsible for the complexity of the evaluation.

Recommendations have been made for changes in procedure which should reduce the total time required for drying certain types of clayware. In addition, the suggested changes should greatly reduce the difficulties encountered in present practice because of condensation of water on the ware in the initial portion of the drying run.

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VIII. ACKNOWLEDGMENT

The author wishes to express his appreciation and thanks for the interest and valuable direction of Dr. A. L. Johnson under whose supervision this research was carried out. Thanks are also extended to Dr. Glenn Murphy for assistance with the theoretical stress analysis.

IX. APPENDIX

A. Sample calculation of moisture gradient.

The drying stresses in the cubes investigated in this work are dependent on the difference in moisture content between the drying surface and the center of the cube. This section illustrates the calculations necessary to determine that gradient from the experimental moisture contents taken as described in the Procedure section.

Curve (1) of Figure 14 is a plot of the raw data of moisture content (dry basis) against distance from the drying surface at the time the first crack was seen. The distances were plotted as the midpoint of the slice taken for moisture determination. It was impossible to measure the moisture content exactly at the surface due to the necessity for making a slice of a finite thickness. Therefore, some means of extrapolating the results to zero distance from the surface had to be devised. To do this the same procedure was followed as that outlined for the function of modulus of elasticity and moisture content. It was discovered that the moisture gradient existing at the time the cracks appeared was, in most cases, of a hyperbolic shape. Table III shows an example of the calculated values necessary to obtain the rectified plot shown in curve (2), Figure 14. Some of the data for other runs did not follow the hyperbolic function quite as well as that of Run 38, but the agreement was considered good in most cases.

Table III

Data for rectified plot of moisture *vs.* distance for Run 38.

Distance x (cm.)	% H_2O M	$(x-x_1)$	$(M-M_1)$	$\left(\frac{x-x_1}{M-M_1}\right)$
0.10[a]	9.00[b]	0	0	--
0.20	10.38	0.10	1.38	0.0725
0.30	11.20	0.20	2.20	0.0909
0.40	11.72	0.30	2.72	0.1103
0.50	12.20	0.40	3.20	0.1250
0.60	12.50	0.50	3.50	0.1430
0.70	12.75	0.60	3.75	0.1600
0.80	12.93	0.70	3.93	0.1780
0.90	13.05	0.80	4.05	0.1975
1.00	13.20	0.90	4.20	0.2140
1.10	13.30	1.00	4.30	0.2315
1.20	13.40	1.10	4.40	0.250
1.30	13.50	1.20	4.50	0.267
1.40	13.60	1.30	4.60	0.283
1.50	13.69	1.40	4.69	0.305
1.60	13.77	1.50	4.77	0.315
1.70	13.85	1.60	4.85	0.330
1.80	13.90	1.70	4.90	0.347

[a] x_1 = 0.10cm.

[b] M_1 = 9.00 % H_2O

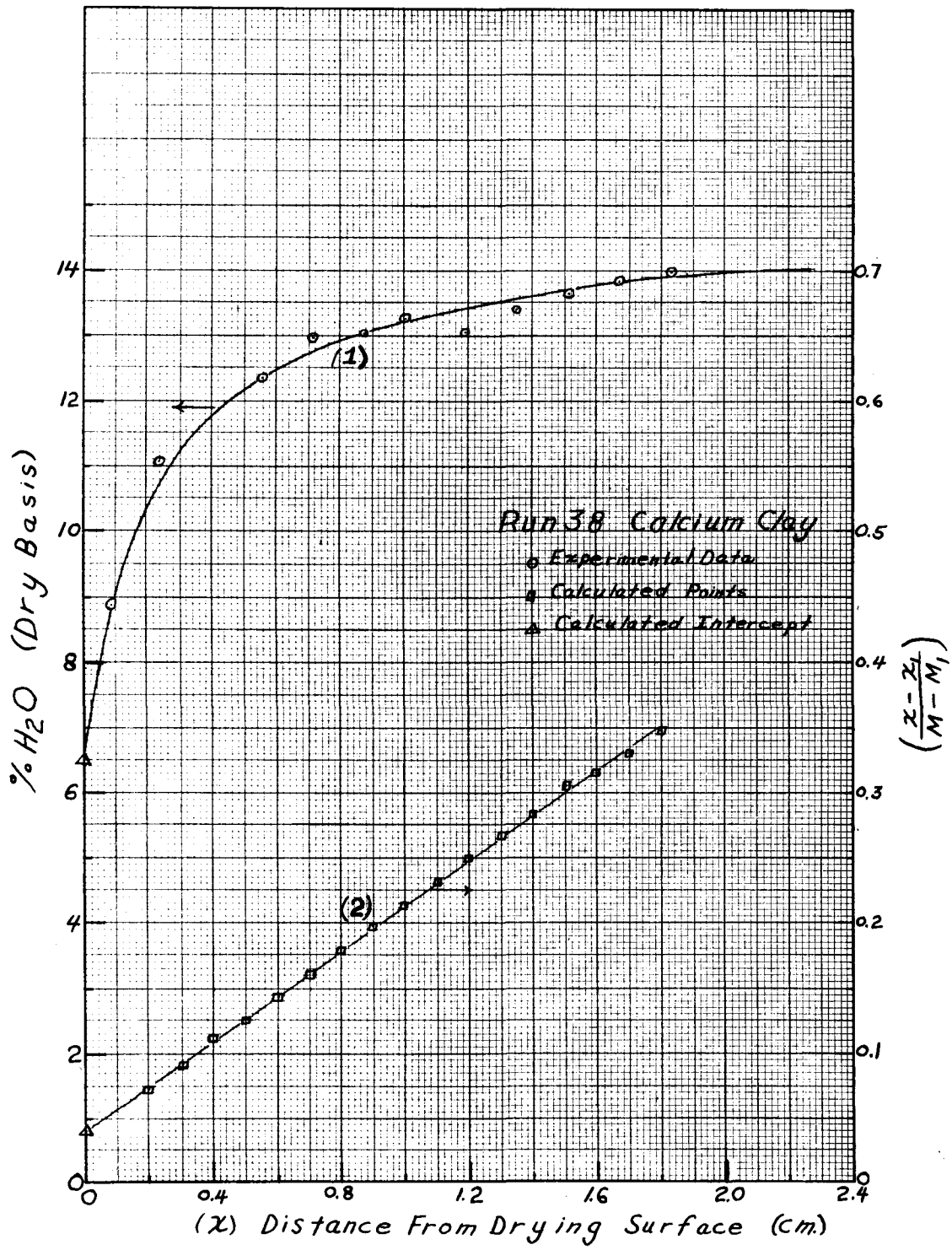

Figure 14. Moisture Gradient (Direct and Rectified)

On curve (2) of Figure 14 we see that when $x = 0$, the term $\left(\frac{x-x_1}{M-M_1}\right) = 0.040$.

Hence, by substitution

$$\left(\frac{0-0.10}{M-9.00}\right) = 0.040$$

$x_1 = 0.10$ cm.

$M_1 = 9.00\%$ H_2O

$M = 6.50\%$ H_2O at the surface of the cube.

The equation of curve (2) may now be written utilizing the standard straight-line equation ($y = mx + b$) where (m) is the slope of the straight line and (b) is the y-intercept.

For this run

$$\left(\frac{x-x_1}{M-M_1}\right) = mx + b = \left(\frac{0.110 - 0.040}{0.40 - 0}\right)x + 0.040$$

$$\left(\frac{x-x_1}{M-M_1}\right) = 0.175x + 0.040 \qquad (1)$$

Rearranging

$$x - 0.175Mx - 0.040M + 0.175(9.00)x + 9.00(0.040) - 0.10 = 0$$

$$2.575x - 0.175Mx - 0.040M + 0.26 = 0$$

Dividing by 2.575 gives the final form of the equation

$$x - 0.0680Mx - 0.0155M + 0.101 = 0 \qquad (2)$$

Equation (1) may now be used to determine the moisture content at the center of the cube by substituting the value $x = 2.54$ cm. Solution of equation (2) under these conditions shows that the moisture content at the center of the cube is

14.01%. This gives a moisture gradient of (14.01% - 6.50%) = 7.51% H_2O.

B. Drying rate.

The drying rate curve in Figure 15 was calculated by standard methods from a plot of weight of the drying cube against time of drying. Run 34, for which the rate is plotted in Figure 15, is typical of those calculated.

C. Thermal analysis.

The photographic record of the thermal analysis mentioned on page 37 is reproduced in Figure 16. A line connecting the zero marks at each end of the scale represents zero difference between the temperature of the reference material and the temperature of the clay sample being tested. If the thermal curve lies above this zero line, it means that an exothermic reaction was taking place. If the thermal curve lies below the zero line, an endothermic reaction was the cause. In addition, there is the possibility of both types of reaction occurring at once with one or the other being dominant. In this case, small dips may appear in the curve without actually crossing the zero line.

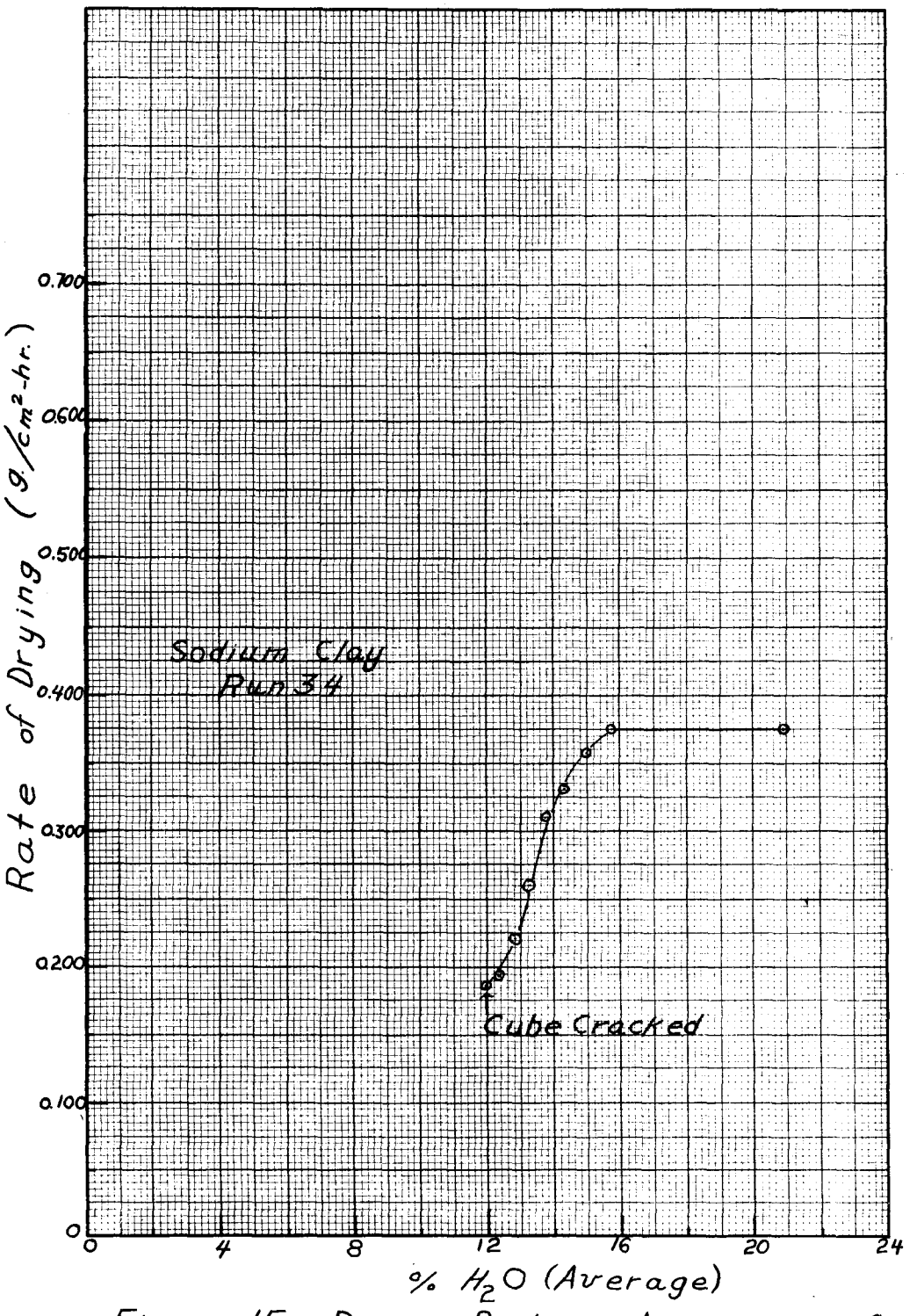

Figure 15. Drying Rate vs. Average % H_2O

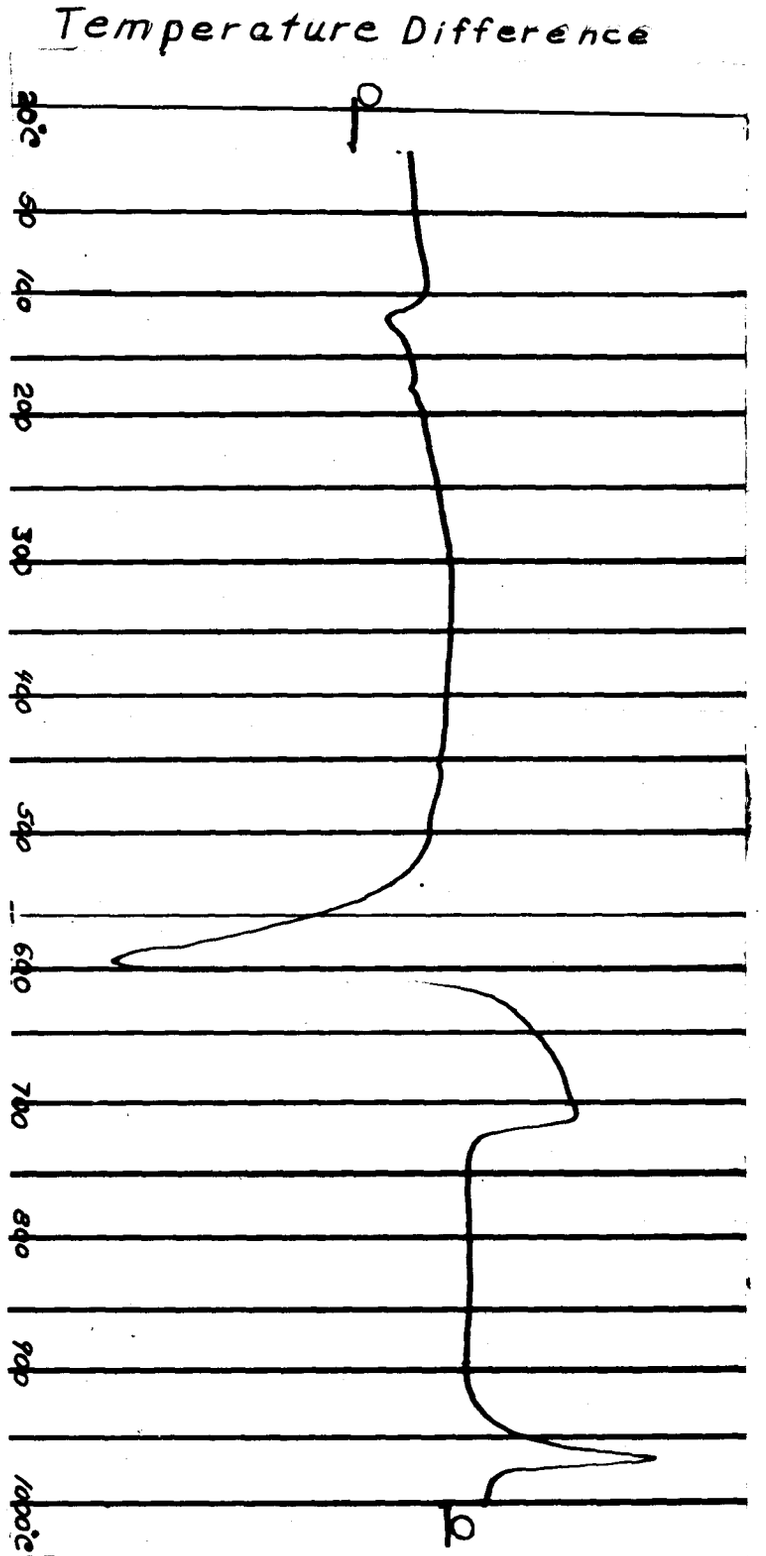

Figure 16. Thermal Analysis

D. Particle size.

The size distribution of particles that passed a 325-mesh screen is shown in Figure 17. The somewhat eccentric shape of the curve at 2 microns and again at 10 microns is probably due to the settling out of the finer particles of flint and feldspar which were present in this commercial body.

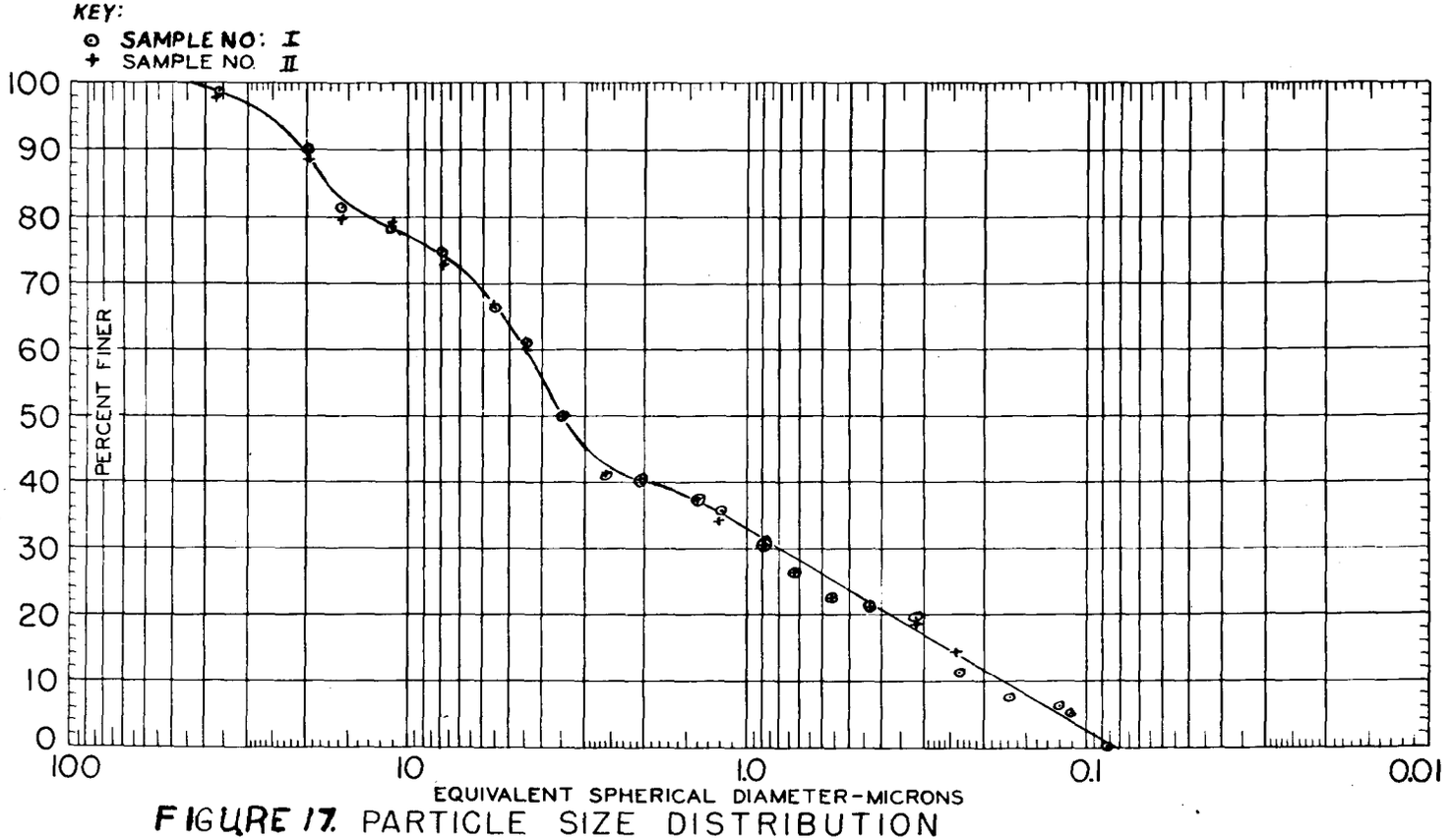

FIGURE 17. PARTICLE SIZE DISTRIBUTION

E. Development of tangential stress equations.[1]

The equations developed herein are admittedly approximations since the assumption is made that the clayware is an elastic body. Actually this is true only for clayware in dry and fired conditions.[2] However, a certain elasticity of action of the material was noted throughout the moisture range investigated in this work as indicated by the shape of the load-deflection diagrams in the modulus of elasticity tests. On the basis of these observations the following equations are presented, admitting they are approximations. It is the hope of the author that they may be useful in estimating drying stresses at a later date when more information is available on the modulus of elasticity and ultimate tensile strength as functions of moisture content.

It was stated on page 57 (see also Figure 9) that a state of equilibrium exists in any spherical shell in the drying sphere of clay between a total radial force acting outward equal to $(S_r \pi r^2)$, a radial force acting inward equal to

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[1]The assistance of Dr. Glenn Murphy of the Iowa State College staff in setting up these equations is gratefully acknowledged and greatly appreciated.

[2]Lassettre, Marjorie and Everhart, J. O., "Stress-Strain Relations in Ceramic Materials", Presented at the Amer. Ceram. Soc. meeting in Buffalo, N. Y., Apr.-May, 1946; Abstracted in Amer. Ceram. Soc. Bull., 25, 139 (1946).

An electric strain gauge was used to study deformation of several types of ceramic materials under stress. It was found that they behaved as elastic materials.

$[(S_r + dS_r)(r + dr)^2 \pi]$ and a tangential force in the shell equal to $(2\pi S_t r dr)$. The equilibrium equation is therefore[1]

$$(2\pi S_t r dr) + (S_r + dS_r)(r + dr)^2 \pi = S_r \pi r^2 \qquad (1)$$

Multiplying where indicated and collecting terms gives

$$2S_t r dr + S_r r^2 + 2S_r r dr + r^2 dS_r = S_r r^2$$

or dividing by (rdr)

$$2S_t + 2S_r + r\frac{dS_r}{dr} = 0 \qquad (2)$$

In multiplying and collecting terms above, the product of two differential terms was considered to be small enough to be negligible and therefore was omitted in the final equilibrium equation (2).

Now, let (u) be the combined radial displacement due to shrinkage and stress of any point in the assumed sphere. Since the ware was dried from all sides[2] we may assume symmetry. Then:

$$\epsilon_r = \frac{du}{dr}\ ; \qquad \epsilon_t = \frac{u}{r} \qquad (3)$$

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[1] See Nomenclature section on page vi for the meaning of symbols employed here.

[2] The drying airstream did not have as free access to the bottom surface of the samples as to the other sides. However, this surface was closest to the heating elements and appeared to be very nearly as dry as the sides and top of the cube throughout the run.

Equations (3) represent the radial and tangential unit displacements respectively. Hooke's law shows that

$$\epsilon_r = \frac{S_r}{E} - \mu\frac{S_t}{E} - \mu\frac{S_t'}{E} + \epsilon_s \qquad (4)$$

$$\epsilon_t = \frac{S_t}{E} - \mu\frac{S_r}{E} - \mu\frac{S_t'}{E} \quad \epsilon_s \qquad (5)$$

In these two equations (4, 5), the terms involving S_r represent unit displacements due to radial stress. Those terms involving S_t and S_t' are unit displacements due to stresses in the two tangential directions. S_t may be considered to be equal to S_t' because of symmetry for the case of the sphere. The last term in equations (4, 5) represents the displacement due to actual shrinkage. Assuming $S_t = S_t'$ and simplifying,

$$\epsilon_r = \frac{S_r}{E} - 2\mu\frac{S_t}{E} + \epsilon_s = \frac{du}{dr} \qquad (4\text{-a})$$

$$\epsilon_t = (1-\mu)\frac{S_t}{E} - \mu\frac{S_r}{E} + \epsilon_s = \frac{u}{r} \qquad (5\text{-a})$$

Use may now be made of equations (4-a) and (5-a) in obtaining an expression for S_t not involving S_r. Solving (4-a) and (5-a) for the term $\left(\frac{\mu S_r}{E}\right)$,

$$\mu\frac{S_r}{E} = \left(\frac{1-\mu}{E}\right)S_t - \frac{u}{r} + \epsilon_s = \mu\frac{du}{dr} \quad 2\mu^2\frac{S_t}{E} - \mu\epsilon_s \qquad (6)$$

Rearranging and solving for S_t

$$S_t = \left[\frac{\frac{u}{r} + \mu\frac{du}{dr} - (1+\mu)\epsilon_s}{1-\mu-2\mu^2}\right] E \qquad (7)$$

Similarly, S_r was found to be

$$S_r = \left[\frac{2\mu\frac{u}{r} + (1-\mu)\frac{du}{dr} - (1+\mu)\epsilon_s}{1-\mu-2\mu^2}\right] E \qquad (8)$$

If the material studied were perfectly elastic, equation (7) could be combined directly with the somewhat similar equation (8) for S_r and with the equilibrium equation (2) to give a second order linear differential equation expressing the radial displacement as a function of the radius (r) of the sphere which could be readily integrated. Once this was done it would be a fairly easy task to calculate corresponding values of $\left(\frac{u}{r}\right)$ and $\left(\frac{du}{dr}\right)$ to use in equation (7) in calculating S_t. However, since the wet clay is not an elastic body the modulus of elasticity (E) appearing in equation (7) must be considered as a function of moisture content (M) which in turn is a function of the radius (r). The relationship between M and (r) may be determined for any specific instant, but no simple expression is available to correlate the two variables throughout the drying operation. In addition, results of the work on modulus of elasticity as a function of moisture content for one clay were not considered conclusive enough for

a basis for a rigorous stress analysis. Poisson's ratio (μ) is also unknown for the wet clay but could be estimated for an approximate calculation.

The equilibrium equation (2) may be combined with equations (7) and (8) and rewritten as

$$2\left[\frac{\frac{u}{r}+\mu\frac{du}{dr}-(1+\mu)\,\epsilon_s}{1-\mu-2\mu^2}\right]f(r)$$

$$+\,2\left[\frac{2\mu\frac{u}{r}+(1-\mu)\frac{du}{dr}-(1+\mu)\,\epsilon_s}{1-\mu-2\mu^2}\right]f(r)$$

$$+\,r\left(\frac{d\left\{\left[\frac{2\mu\frac{u}{r}+(1-\mu)\frac{du}{dr}-(1+\mu)\,\epsilon_s}{1-\mu-2\mu^2}\right]f(r)\right\}}{dr}\right)=0 \qquad (9)$$

where f(r) is used to replace E. As stated above, when enough experimental data is available to justify a substitution of a definite function of the radius (r) for the modulus of elasticity, then equation (9) may be integrated, if possible, and the resulting function of (u) and (r) used to calculate the theoretical tangential stress distribution in drying clayware.

Investigation along this line using the data relating E,

M and (r) obtained by the author resulted in an equilibrium equation which could not be integrated by standard analytical or graphical means.